

NPL REPORT ENV 8

**DIFFERENTIAL ABSORPTION LIDAR (DIAL) QUANTIFICATION OF
BENZENE AND VOC FUGITIVE EMISSIONS FROM A REFINERY
TANK FARM IN LOS ANGELES, USA, SEPTEMBER-OCTOBER 2015**

**F INNOCENTI
R A ROBINSON
T D GARDINER
A J FINLAYSON**

APRIL 2017

Differential Absorption Lidar (DIAL) Quantification of Benzene and VOC
Fugitive Emissions from a Refinery Tank Farm in Los Angeles, USA,
September-October 2015

F Innocenti, R A Robinson, T D Gardiner and A J Finlayson
Environment Division

ABSTRACT

This report presents the results of benzene and non-methane VOC emission measurements from a refinery in Los Angeles, USA, carried out using the NPL Differential Absorption Lidar (DIAL). The measurements were conducted between September 28 and October 7, 2015

© NPL Management Limited, 2016

ISSN 2059-6030

National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

Extracts from this report may be reproduced provided the source is acknowledged
and the extract is not taken out of context.

Approved on behalf of NPLML by
Martyn Sene, Director, Operations Division.

CONTENTS

TABLES	I
FIGURES	II
EXECUTIVE SUMMARY	III
1 INTRODUCTION	1
2 OVERVIEW OF DIAL MEASUREMENT TECHNIQUE AND METHOD.....	3
2.1 THE DIAL TECHNIQUE.....	3
2.2 DIAL TRAILER LOCATION	3
2.3 LINES-OF-SIGHT AND NUMBER OF SCANS	4
2.4 EMISSIONS FROM DIFFERENT AREAS OF THE SITE	4
2.5 METEOROLOGICAL MEASUREMENT	5
2.6 OUTPUT.....	5
2.7 CALIBRATION PROCEDURE.....	6
2.8 MEASUREMENT UNCERTAINTY	6
3 OVERVIEW OF MEASUREMENT APPROACH	7
3.1 FLUX DETERMINATION APPROACH.....	9
4 SUMMARY TABLES AND FIGURES.....	10
5 RESULTS DISCUSSION FOR BENZENE MEASUREMENTS.....	33
5.1 MEASUREMENTS OF THE SOUTH TANK AREA	33
5.2 MEASUREMENTS OF THE NORTH TANK AREA.....	33
5.3 CONCLUSION	34
6 RESULTS DISCUSSION FOR VOC MEASUREMENTS	35
6.1 MEASUREMENTS OF RESERVOIR 502.....	35
6.2 MEASUREMENTS OF TANK 16.....	36
6.3 MEASUREMENTS OF OTHER TANKS IN THE NORTH AREA.....	38
6.4 MEASUREMENTS OF THE SOUTH PART OF THE TANK PARK AREA	38
6.5 CONCLUSION	39
7 CONCLUSIONS.....	41
8 REFERNCES.....	43
9 APPENDIX 1: DESCRIPTION OF THE DIAL TECHNIQUE	44
9.1 OVERVIEW OF THE DIAL TECHNIQUE	44
9.2 DESCRIPTION OF THE THEORY OF DIAL MEASUREMENTS.....	44
9.3 DESCRIPTION OF FACILITY OPERATED BY NPL.....	45
9.4 GENERAL HYDROCARBON SCALING FACTOR	48
9.5 RELATIONSHIP BETWEEN EMISSION RATE AND CONCENTRATIONS	48

9.6	CALIBRATION AND VALIDATION	49
9.7	NPL OPEN-PATH CALIBRATION FACILITY	50
10	APPENDIX 2: VOC SPECIATION USING PUMPED SORPTION TUBES.....	52
10.1	SPECIATION RESULTS FROM THE ATD TUBE SAMPLES	53

TABLES

Table ES.1 Hourly average benzene emission rates measured during September 28-29 DIAL survey.	iii
Table ES.2 Hourly average VOC emissions detected during October 1-7 DIAL survey.	iv
Table 3.1 Summary of DIAL measurement locations.	7
Table 4.1 Benzene Emission rate determined from TB01 on 28 th of September.	11
Table 4.2 Benzene Emission rate determined from TB02 on 29 th of September.	13
Table 4.3 Benzene Emission rate determined from TB03 on 29 th of September.	14
Table 4.4 Benzene Emission rate determined from TB04 on 29 th of September.	15
Table 4.5 Benzene Emission rate determined from TB05 on 29 th of September.	16
Table 4.6 VOC Emission rate determined from TV01 on 1 st of October.	17
Table 4.7 VOC Emission rate determined from TV02 on 1 st of October.	19
Table 4.8 VOC Emission rate determined from TV03 on 2 nd of October.	20
Table 4.9 VOC Emission rate determined from TV04 on 2 nd of October.	21
Table 4.10 VOC Emission rate determined from TV05 on 2 nd of October.	23
Table 4.11 VOC Emission rate determined from TV06 on 5 th of October.	24
Table 4.12 VOC Emission rate determined from TV07 on 5 th of October.	25
Table 4.13 VOC Emission rate determined from TV08 on 6 th of October.	27
Table 4.14 VOC Emission rate determined from TV09 on 6 th of October.	28
Table 4.15 VOC Emission rate determined from TV10 on 7 th of October.	30
Table 4.16 VOC Emission rate determined from TV11 on 7 th of October.	31
Table 5.1 Summary of determined benzene emission rates. For each location and LOS the average flux and standard deviation (when more than one scan is available) are reported.	33
Table 5.2 Summary of benzene flux measurements for different site's areas.	34
Table 6.1 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation (when more than one scan is available) are reported.	35
Table 4.2 Summary of VOC flux measurements for different areas of a tank farm.	39
Table A1.1 Ultraviolet capability of NPL DIAL Facility	47
Table A1.2 Infrared capability of NPL DIAL Facility	47

FIGURES

Figure 1.1 NPL DIAL facility on a site.....	1
Figure 2.1a Measurement of emissions from two DIAL locations.	3
Figure 2.1b Measurement of emissions from one DIAL location.....	4
Figure 2.2 DIAL Measurement Configuration.....	5
Figure 3.1 DIAL benzene measurement locations.....	7
Figure 3.2 DIAL VOC measurement locations.....	8
Figure 3.3 Wind rose during DIAL measurement periods from 28 th September to 7 th October	9
Figure 4.1 Measurement configuration for location TB01 on 28 th of September.	11
Figure 4.1a1 Observed benzene concentration for Scan 6 representing TB01/LOS1.....	12
Figure 4.1a2 Visualisation of emission rate for Scan 6 representing TB01/LOS1.	12
Figure 4.2 Measurement configuration for location TB02 on 29 th of September.	13
Figure 4.3 Measurement configuration for location TB03 on 29 th of September.	14
Figure 4.4 Measurement configuration for location TB04 on 29 th of September.	15
Figure 4.5 Measurement configuration for location TB05 on 29 th of September.	16
Figure 4.6 Measurement configuration for location TV01 on 1 st of October.....	17
Figure 4.6a1 Observed VOC concentration for Scan 30 representing TV01/LOS1.	18
Figure 4.6a2 Visualisation of emission rate for Scan 30 representing TV01/LOS1.	18
Figure 4.7 Measurement configuration for location TV02 on 1 st of October.....	19
Figure 4.8 Measurement configuration for location TV03 on 2 nd of October.....	20
Figure 4.9 Measurement configuration for location TV04 on 2 nd of October.....	21
Figure 4.9a1 Observed VOC concentration for Scan 59 representing TV04/LOS2.	22
Figure 4.9a2 Visualisation of emission rate for Scan 59 representing TV04/LOS2.	22
Figure 4.10 Measurement configuration for location TV05 on 2 nd of October.....	23
Figure 4.11 Measurement configuration for location TV06 on 5 th of October.	24
Figure 4.12 Measurement configuration for location TV07 on 5 th of October.	25
Figure 4.12a1 Observed VOC concentration for Scan 85 representing TV07/LOS1.	26
Figure 4.12a2 Visualisation of emission rate for Scan 85 representing TV07/LOS1.	26
Figure 4.13 Measurement configuration for location TV08 on 6 th of October.	27
Figure 4.14 Measurement configuration for location TV09 on 6 th of October.	28
Figure 4.14a1 Observed VOC concentration for Scan 106 representing TV09/LOS1.	29
Figure 4.14a2 Visualisation of emission rate for Scan 106 representing TV09/LOS1.	29
Figure 4.15 Measurement configuration for location TV10 on 7 th of October.	30
Figure 4.16 Measurement configuration for location TV11 on 7 th of October.	31
Figure 4.16a1 Observed VOC concentration for Scan 130 representing TV11/LOS2.	32
Figure 4.16a2 Visualisation of emission rate for Scan 130 representing TV11/LOS2.	32
Figure 6.1 VOC emission rate from Tank 16.....	37
Figure A1.1 Illustration of the emission rate calculation approach.....	48
Figure A1.2 Schematic showing relationship between emission rate and wind direction	49
Figure A1.3 The NPL 10 m calibration cell.	50
Figure A2.1 Pumped sample tube locations during the tank farm campaign.....	52
Figure A2.2 Volume fraction of VOCs in the four samples.....	54

EXECUTIVE SUMMARY

Background

Refineries are key contributors to the stationary source emission inventory in the South Coast Air Basin (SCAB). However, their emissions are not fully characterized and the air quality in the SCAB remains among the worst in the USA. Thus, characterizing the actual magnitude of volatile organic compounds (VOCs) and other hazardous air pollutants (HAPs) emissions is crucial for attaining EPA air quality standards and for improving the well-being of people living in the SCAB. Optical remote sensing (ORS) methods, such as Differential Absorption Lidar (DIAL), offer a powerful set of capabilities for identifying, mapping and quantifying a wide range of emissions.

During the past few years the South Coast Air Quality Management District (SCAQMD) has been developing a fence line monitoring program to better characterize and quantify actual VOC emissions from large petrochemical facilities in the SCAB. As part of this program, different contractors and vendors were selected to conduct measurements of VOC emissions from refineries using a variety of ORS methods. The National Physical Laboratory (NPL) was selected to conduct emission measurements of VOCs and benzene from specific areas of a refinery using the DIAL method. This measurement survey was carried out between September 28 and October 7, 2015. In addition, NPL conducted a direct intercomparison with other optical remote techniques involved in the project by performing measurements of the same emission sources at the same time.

Method

DIAL is a well-established and proven ORS technique that has been used by NPL in numerous emission surveys around the globe [e.g. Robinson et al., 2011]. The DIAL method allows to make spatially resolved concentration measurements of a target gas along the path of an eye-safe laser beam transmitted into the atmosphere. During the measurement, the laser is operated alternately at two adjacent carefully chosen wavelengths. One, called the ‘on-resonant wavelength’, is a wavelength which is absorbed by the target species. The other, the ‘off-resonant wavelength’, is a wavelength which is not absorbed significantly by the target species. The difference in the absorption of the two wavelengths is related to the concentration of the gas. Spatial resolution is obtained by pulsing the laser beam. Ultimately, emissions fluxes are determined by scanning the laser beam through the atmosphere to build up a concentration map, and combining this with measurements of the wind speed and direction.

Results and Discussion

DIAL benzene measurements at a tank farm were carried out on September 28-29, 2015. During this short period we surveyed the majority of the tank farm area. Benzene emissions from a number of tanks in the south and north-east parts of the farm were investigated in detail. Overall, the total emission rate from these areas was found to be 1.2 ± 0.3 kg/hr. Table ES.1 provides the average hourly benzene emission rates measured from different parts of the tank farm. The south-east part of the tank farm made the largest contribution to the total emission, with 0.6 ± 0.3 kg/hr of benzene emission detected from the cluster of tanks 11, 19 through 24, and 83. Other measured tank clusters in the southern and north-eastern parts of the tank farm contributed the second half of the measured emission, with average emission rates of 0.1 - 0.2 kg/h.

Table ES.1 Hourly average benzene emission rates measured during September 28-29 DIAL survey.

Emission Area	Average Flux	Standard Deviation
	kg/hr	kg/hr
Tanks 42,52,66,53,67,54,68,69	0.2	0.1
Tanks 90,91,93	0.1	-
Tanks 33,34,35,43,44,45	0.1	-
Tanks 11,21,22,23,24,19,20,83	0.6	0.3
Tanks 26,16,17 & Central Area 502	0.2	0.0
Total	1.2	0.3

DIAL VOC measurements of the tank farm area were conducted from October 1 through October 7, 2015. During these four and a half days of monitoring about half of the time was dedicated to repeat measurements of the same sources in order to carry out direct intercomparison data with other ORS techniques involved in the project. For this purpose, emissions from Reservoir 502 were measured on several occasions on different days. Emissions from Tank 16 were also conducted during a high emission leak event that occurred on the October 5. The rest of the time was used to determine emission rates from as much of the tank farm area as possible. At the end of this measurement campaign, we were able to measure emissions from a substantial portion of the tank area. Although a few NE tanks were not covered by our measurements, our best estimate of the total emission from the tank farm area is 194.4 ± 19.4 kg/hr. Table ES.2 shows average hourly VOC emissions from different parts of the tank farm.

Table ES.2 Hourly average VOC emissions detected during October 1-7 DIAL survey.

Emission Area	Average Flux	Standard Deviation
	kg/hr	kg/hr
Tanks 68,69,90,91,93 + NW Small Tanks	28.1	1.6
Tanks 34,33,20,19	10.9	-
Tanks 53,54,55,56,57,58,43,44,45	20.7	5.1
Tanks 58 & 59	7.3	0.9
Reservoir 502	49.7	12.7
Tanks 29,30,31,26,16,17,6	13.2	2.1
Tanks 11,12,13,14,21,22,23,24, 25	63.0	13.5
Tanks 3, 4	1.5	-
Total	194.4	19.4

The highest average VOC emission rate of 63 ± 13.5 kg/hr was measured from the cluster of tanks 11 through 15 and 21 through 25 located in the south-east part of the tank farm. The south vent of Reservoir 502 was found to be the single highest continuous emission source (VOC emissions detected during all samples), with total emission varying from 30 kg/hr to 70 kg/hr during the measurement period.

The leak event from Tank 16 on October 5 was measured from two different locations, and a total of twelve scans were made. Eleven of these scans showed a stable emission rate with an average of 270.1 ± 20.4 kg/hr, while one scan showed a higher emission rate of about 400 kg/hr. DIAL and other ORS methods were able to detect the Tank 16 leak in real-time. As a result refinery personnel were alerted immediately and the main cause of the leak was promptly identified and repaired the same day.

The reported 2015 annual VOC and benzene emissions for the entire refinery site were equivalent to an average hourly emission of 45.6 kg/hr and 0.08 kg/hr respectively [SCAQMD FIND, 2016]. These values are about a factor 4 for VOC and 10 for benzene lower than the emission observed by the DIAL during the six measurement days at the facility's tank farm. Such comparison can only be valid if the emission rate measured during a short study was representative of the average annual emissions. Since the emission rates could vary during the year, longer measurements over different periods would be informative to obtain a more accurate comparison between measured and annual reported emissions. It should also be noted that these DIAL emission factors are solely based on a limited set of emissions measurements conducted in only one area of the refinery, and excluded contributions from the Tank 16 leak event. Since any area that is not measured could only increase or maintain the total emission when measured, it is possible for the actual discrepancy between measured and reported VOC and benzene emissions to be even greater than what was observed in this study.

Overall, this work provided SCAQMD with enhanced actual emission data with low detection limits and high temporal resolution. This will greatly contribute to improve emission inventory estimates by narrowing the gap between measured and reported fugitive emission levels from refineries. During this survey we noticed that the majority of VOC emissions originated from a very few sources within the

tank farm area such as Reservoir 502 and the SE tanks, particularly Tanks 12 and 13. Therefore, significant emission reduction can be achieved by minimizing emissions from the identified sources. Moving forward, comprehensive ORS surveys repeated over time can lead to significant emission reductions as well as to improved emissions factors. Finally, real-time detection of the Tank 16 leak and resulting repairs serve as an example of improved leak-detection capabilities provided by ORS technologies in comparison to currently adopted LDAR methods.

1 INTRODUCTION

This report presents the results of a measurement campaign carried out using the National Physical Laboratory's (NPL) Differential Absorption Lidar (DIAL) system (shown in Figure 1.1) to monitor emission rates of benzene and non-methane VOCs (referred only as VOC in the rest of the document) from a refinery tank farm site in Los Angeles, USA, in September/October 2015. Measurements were performed as a part of South Coast Air Quality Management District (SCAQMD) project "Quantification of Fugitive Emissions from Large Refineries" aimed to quantify actual emissions from large petrochemical facilities in the South Coast Air Basin (SCAB). NPL was selected to conduct emission measurements as well as validation and intercomparison work using the DIAL method. VOC and benzene surveys of the storage tank area of a refinery in the SCAB were carried out between September 28 and October 7, 2015.



Figure 1.1 NPL DIAL facility on a site.

Refineries play a crucial role in determining air quality in the South Coast Air Basin (SCAB). However, their emissions are not fully characterized and the air quality in the SCAB remains among the worst in USA. Thus, characterizing the actual magnitude of emissions of VOCs and other harmful air pollutants (HAPs) is crucial for attaining EPA air quality standards and for improving the well-being of people living in the SCAB. DIAL and other optical remote sensing (ORS) methods offer a powerful set of capabilities for identifying, mapping and quantifying a wide range of emissions. The successful deployment and implementation of these ORS techniques will establish SCAQMD as the first air monitoring agency in USA with such capabilities. Enhanced monitoring capabilities will greatly contribute to improving emission inventory estimates by narrowing the gap between measured and reported fugitive emission levels from refineries.

The primary objectives of the study were to characterise and quantify emissions from a refinery tank farm and to carry out direct intercomparison measurements with other optical remote techniques involved in the project by performing measurements of the same emission sources at the same time.

An overview of the DIAL technique is given in Section 2. A brief overview of the measurement approach and the DIAL measurement locations used during the campaign is given in Section 3. Section 4 presents summary tables and figures for each day of measurement. Section 5 and 6 present a discussion of the results for the benzene and VOC emission rate measurements respectively. Technical details for the measurement methodology are presented in Appendix 1, which provides an overview of the DIAL technique, and discusses the calibration and validation procedures. Appendix 2 presents the results of speciation measurements of air samples using pumped absorption tubes.

2 OVERVIEW OF DIAL MEASUREMENT TECHNIQUE AND METHOD

This section describes the principles for applying the DIAL technique, a more detailed description of the DIAL methodology can be found in Appendix 1.

2.1 THE DIAL TECHNIQUE

The DIAL technique is a remote sensing method capable of making spatially resolved measurements of concentrations of a target gas (in this case either VOC or benzene) along the path of an eye-safe laser beam transmitted into the atmosphere. The method is outlined below with a more detailed description provided in Appendix 1.

In the DIAL technique, the laser is operated alternately at two adjacent wavelengths. One of these, the 'on-resonant wavelength', is chosen to be at a wavelength which is absorbed by the target species. The other, the 'off-resonant wavelength', is chosen to be a wavelength which is not absorbed significantly by the target species. The difference in the absorption of the two wavelengths allows the concentration of the gas to be calculated. Spatial resolution is obtained by pulsing the laser beam in the 200 nm and 3.3 μm regions for benzene and VOC respectively.

Emissions fluxes are determined by scanning the laser beam through the atmosphere to build up a concentration map, and combining this with measurements of the wind speed and direction.

2.2 DIAL TRAILER LOCATION

To measure the flux from an identified source, the DIAL is first placed so that a series of downwind scans can be obtained, and then, if possible, DIAL is moved to another position to monitor the upwind flux (Figure 2.1a). In some cases upwind and downwind fluxes can be obtained from a single location (Figure 2.1b). In order to perform measurements, the DIAL has to 'stand-off' by a minimum measurement distance of 50m (that is measurements cannot be undertaken in the first 50m from the Trailer); the DIAL does not have to be located in the emissions plume.

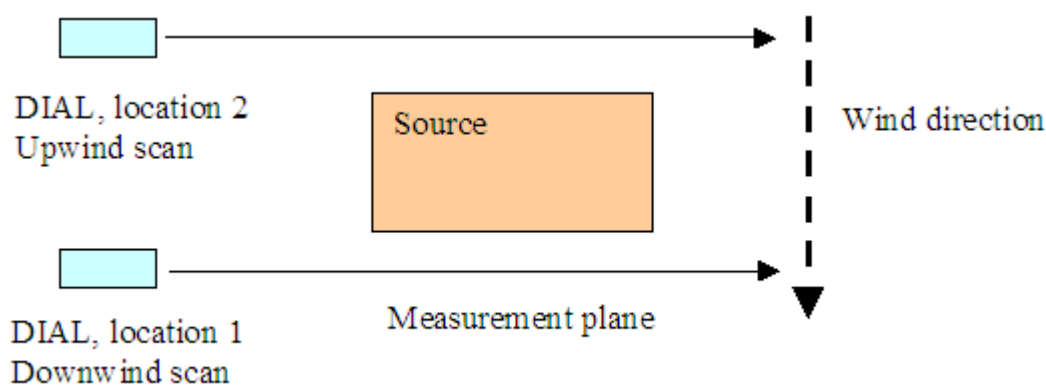


Figure 2.1a Measurement of emissions from two DIAL locations.

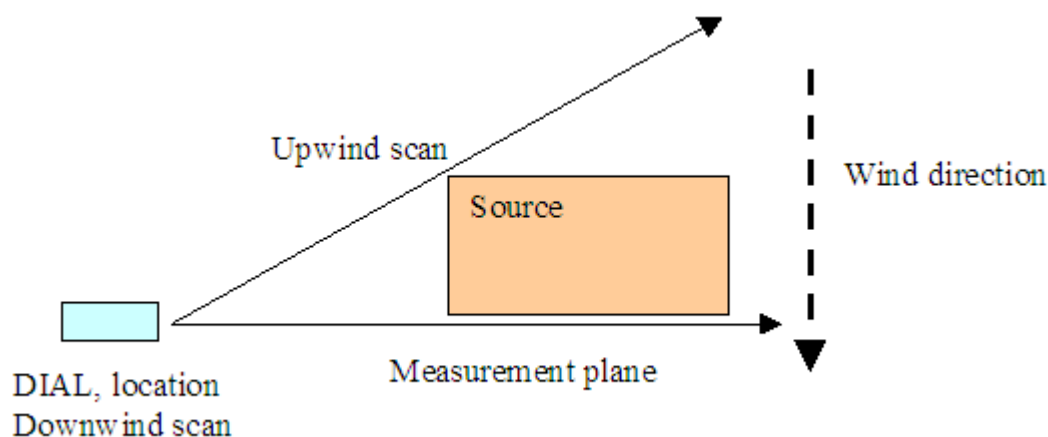


Figure 2.1b Measurement of emissions from one DIAL location.

For each source, the DIAL placement location is chosen by taking into consideration the availability of unobstructed view of the different areas of site and the current wind direction. The DIAL can be moved during the day if the wind direction changes and if different areas of the site can be measured from other locations.

The maximum scan range of the DIAL system depends on the atmospheric conditions, and therefore varies from day to day and can also change throughout the day, however, for VOC the range is typically between 400 m and 1 km. The strength of the returning DIAL radiation depends on atmospheric conditions as the transmitted infrared radiation is returned by scattering from aerosol/dust particles in the atmosphere.

As the suitability of a measurement location is dependent on wind direction, the choice of measurement locations at the tank farm was made on the day every day. The aim was to get measurements of most of the tank farm emission in the allowed time. Due to the flexibility of the DIAL scanning equipment, measurements could be made along different directions from most of the locations, therefore allowing for sampling of almost entire area of the tank farm in a very short period of time.

2.3 LINES-OF-SIGHT AND NUMBER OF SCANS

From each location, DIAL scans are normally carried out using different lines-of-sight (LOS) in order to perform downwind and upwind measurements when necessary, which is illustrated in Figure 2.1b, and to have different cuts through the area of interest. In general at least four scans (individual sets of measurements) are made along each LOS. The majority of the scans recorded during a DIAL campaign are downwind of different areas of the site. The rest of the scans are upwind and background measurements.

At the tank farm, scans LOS were chosen at each measurement location to be between 30 and 150 degrees to the wind direction. Quantified fluxes of VOC and benzene were obtained using downwind vertical scans. Whole site emissions were obtained by summing the emissions from individual parts of the site.

2.4 EMISSIONS FROM DIFFERENT AREAS OF THE SITE

Emissions from other areas of the refinery that may have been upwind of the measured sources and therefore contributing to the measured emission fluxes. However, generally these sources were excluded in three ways.

- 1) If the upwind sources to be excluded were close to the measured sources and produced localised plumes, these were discriminated spatially from the measured rates by selecting the regions of the scanned region to integrate, in order to calculate the emission rate only from the area of interest.
- 2) Conversely, if the upwind sources could not be spatially discriminated and the emissions from them have been measured separately in upwind scans then these values were subtracted from the downwind emission rate.
- 3) If the upwind sources were further away (more than 500 - 700 m) and relatively low, they normally would be diffuse and below the measurement noise or detection limit.

In this report, when the first technique was used, it is normally specified which analysis range has been used. When the second technique was used, the value from the subtraction of an upwind emission from a downwind emission rate and its standard deviation are reported.

2.5 METEOROLOGICAL MEASUREMENT

The location of meteorological monitoring stations is usually determined in advance of arriving at the site by examining the local meteorology historical data. For this campaign, the fixed mast, located just outside the site to the north of the tank area, supported four wind sensor packages at 11.9 m, 9.0 m, 6.2 m and 3.4 m elevation from the ground. Additionally, a portable mast that operates at about 2.3 m height was also deployed near the DIAL truck or along the measurement line-of-sight. The DIAL truck was equipped with a met mast that operated at a height of 12 m. The fixed masts wind sensors were calibrated Vector Instrument wind vanes and cup anemometers. These instruments were also checked prior to deployment. Wind data were recorded using battery powered loggers, with two second sampling. The meteorological data were then processed to provide vector averaged wind data for the periods of each DIAL scan. The wind speed data is used to construct a logarithmic wind profile as described in Appendix 1 (section 3).

2.6 OUTPUT

Range-resolved remote DIAL measurements enable total site emissions and area-specific emissions to be measured, with no disruption to normal operational activities. The DIAL data quantify emission rates in kg/hr and provide 2D/3D mapping of emission concentrations in ppm, as illustrated in Figure 2.2.

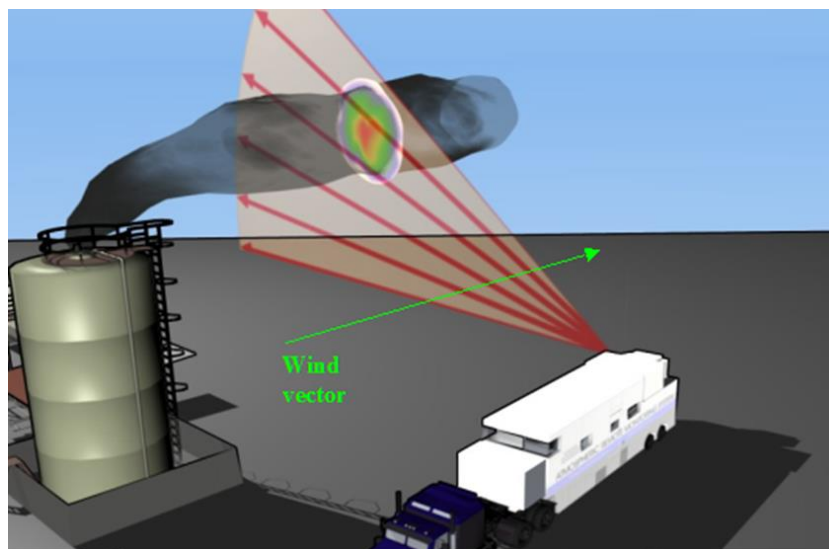


Figure 2.2 DIAL Measurement Configuration.

2.7 CALIBRATION PROCEDURE

The NPL DIAL system has several in-built calibration techniques and procedures. The most important are the in-line gas calibration cells. The gas cells were filled with known concentrations of the target species, from NPL standard gas mixtures, which are directly traceable to national standards. A fraction of the transmitted beam was split off and half was directed straight to a detector, the other half was directed through the gas cell and then onto a detector. This provided a direct measurement of the differential absorption at the operating wavelengths. The ratio between the energy on each detector was continuously monitored during the operation of the system to detect any possible drift in the laser wavelengths. Additionally, once a day the wavelength was scanned through the absorption peak of VOC or benzene and then tuned to appropriate wavelengths for DIAL measurements. The calibration cells were also periodically placed in the output beam to check that the concentration response of the whole system was as expected.

2.8 MEASUREMENT UNCERTAINTY

In previous NPL validation studies, DIAL measurements of total flux have shown agreement with known emission sources of between 5 - 20% (Robinson et al., 2011). The uncertainty of the measurements in this study was estimated based on the standard deviation of the individual flux measurements from which each mean flux value has been determined. As part of this project SCAQMD carried out ten blind controlled releases and the DIAL demonstrated to be very accurate. The differences between the average DIAL and controlled release rates were between -17% (underestimate) and 10% (overestimate) and in four sets of controlled releases this difference was less than 5%.

The DIAL estimated uncertainty for a single measurement is about 20-30%, some of this uncertainty will be included in the reported standard deviation but it is not known how much. The uncertainty reported is the variability of the measured results. As such it encapsulates variability occurring during the measurements – such variability will include the measurement itself (random DIAL measurement uncertainty), variability in the source emissions, and variability in the wind direction and speed used since for each scan a different wind profile is calculated from the wind mast data.

3 OVERVIEW OF MEASUREMENT APPROACH

The NPL DIAL measurements were conducted from a series of locations at the tank farm in order to determine benzene and VOC emission rates from different areas of the site. Table 3.1 lists these DIAL measurement locations and provides the GPS locations for each position. These locations and the different areas of the site are shown in Figure 3.1 and 3.2 for benzene and VOC measurements respectively.

Table 3.1 Summary of DIAL measurement locations.

DIAL Location	Description	GPS Position
TB01	On Corner East of Tank 1	33° 48' 30.94" N , 118° 14' 33.42" W
TB02	Parking Area to E of Tank 95	33° 49' 2.94" N , 118° 14' 48.73" W
TB03	On 300th Ave S of Tank 19	33° 48' 40.41" N , 118° 14' 42.90" W
TB04	NW of Tank 24	33° 48' 41.19" N , 118° 14' 50.97" W
TB05	On 400th Ave by Tank 32	33° 48' 44.30" N , 118° 14' 38.88" W
TV01	South of Tank 60	33° 48' 44.70" N , 118° 15' 5.37" W
TV02	NE of Reservoir 502	33° 48' 43.60" N , 118° 15' 0.97" W
TV03	East of Tank 27	33° 48' 40.76" N , 118° 14' 51.01" W
TV04	South Tank 55	33° 48' 49.44" N , 118° 14' 50.98" W
TV05	North of Tank 66	33° 48' 54.51" N , 118° 14' 42.97" W
TV06	East of tank 27	33° 48' 40.78" N , 118° 14' 51.03" W
TV07	East of Reservoir 502	33° 48' 38.49" N , 118° 15' 1.60" W
TV08	East of Reservoir 502	33° 48' 38.45" N , 118° 15' 1.61" W
TV09	On Corner East of Tank 1	33° 48' 31.01" N , 118° 14' 33.39" W
TV10	West of Tank 20	33° 48' 40.93" N , 118° 14' 50.50" W
TV11	NW of Reservoir 502	33° 48' 40.93" N , 118° 15' 0.44" W

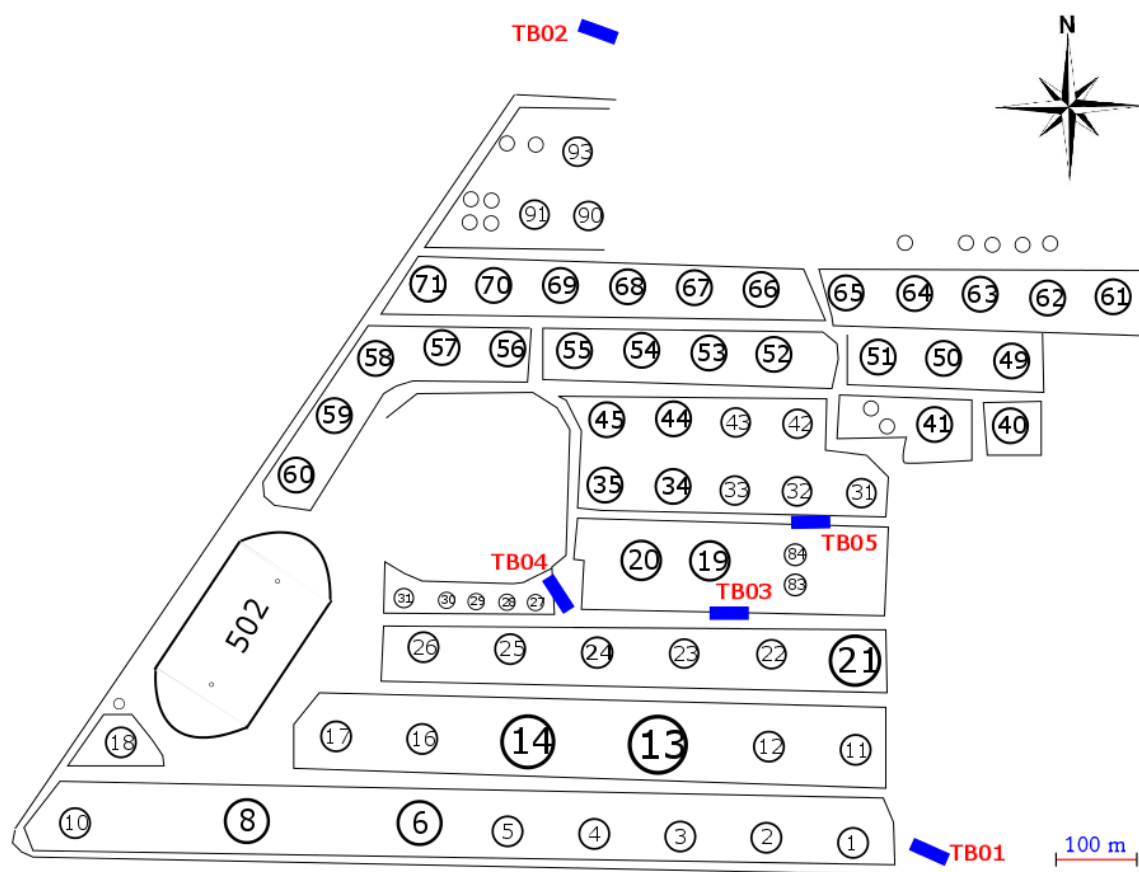


Figure 3.1 DIAL benzene measurement locations

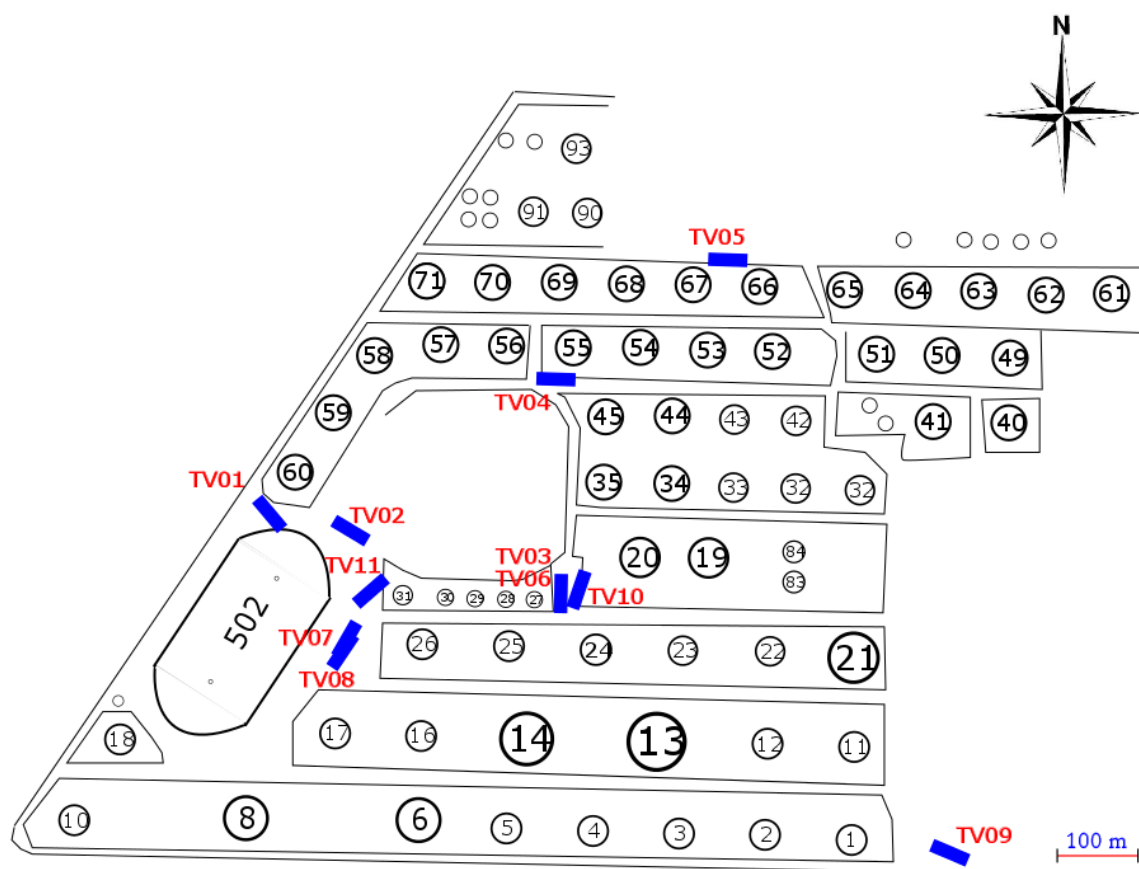


Figure 3.2 DIAL VOC measurement locations

Emission rates were determined using the procedure described in sections 2.2 - 2.3 and Appendix 1, by scanning the DIAL measurement beam in a vertical plane downwind of the target sources, and measuring the total concentration of benzene and VOC in that plane. DIAL VOC measurement is targeted on C2+ hydrocarbons with a standard absorption coefficient based on gasoline vapour. A scaling factor to go from the standard DIAL VOC coefficients to the measured mixtures is then applied based on the results of absorption tube analysis as described in Appendix 2. All the VOC data presented in this report has been corrected using the appropriate scaling factors as described in Appendix 2 and the scaling factor uncertainties have been propagated in quadrature for all the standard deviations presented.

The logarithmic wind field profile used for the emission rate calculations (see Appendix 1) was determined from the speeds on the fixed mast sensors and the portable wind sensor placed on site near each DIAL measurement location. The wind direction measured from the portable and DIAL wind sensors were used to define the wind direction for the emission rate measurements. During the seven measurement days the wind speed was generally low with variable wind direction in the mornings. In the afternoons the wind speed increased and the wind direction was predominantly from the west. Figure 3.3 shows the average wind rose measured from the top sensor of the mast during the DIAL measurement periods from the 28th of September to the 7th of October.

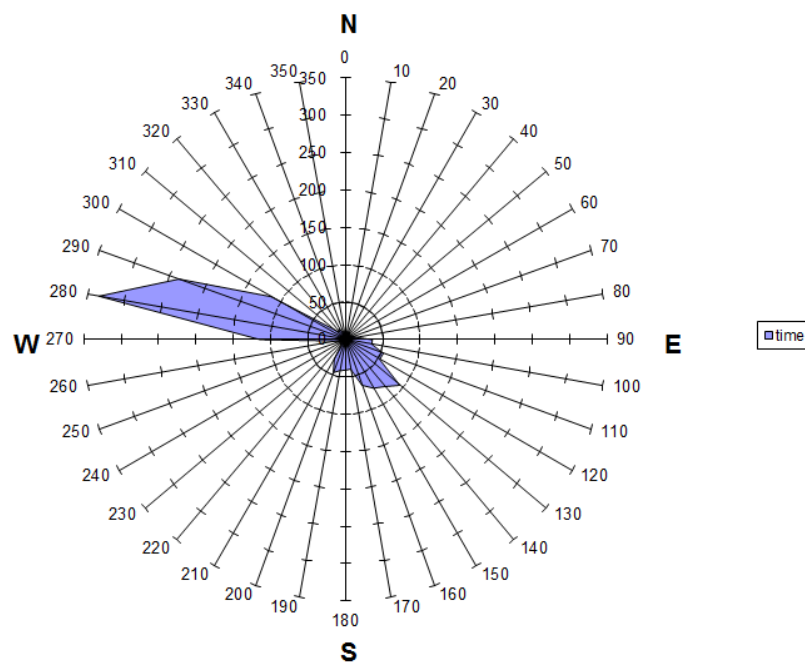


Figure 3.3 Wind rose during DIAL measurement periods from 28th September to 7th October

3.1 FLUX DETERMINATION APPROACH

Emission fluxes of VOC and Benzene from tanks of the refinery tank farm were calculated using approach described in Section 2 and Appendix 1.

Tables 5.1 and 6.1 present the mean and standard deviation of the benzene and VOC emission rates determined from each location for each LOS. The standard deviation values includes the effects of the source variability, DIAL measurement uncertainty and the influence of other factors such as the wind speed and direction variability during the course of individual measurements.

Because the DIAL flux measurement depends on several different experimental conditions, the detection limit can be experimentally estimated when the measured standard deviation is similar to the measured value. The standard deviation therefore defines the detection limit for a given set of measurements.

4 SUMMARY TABLES AND FIGURES

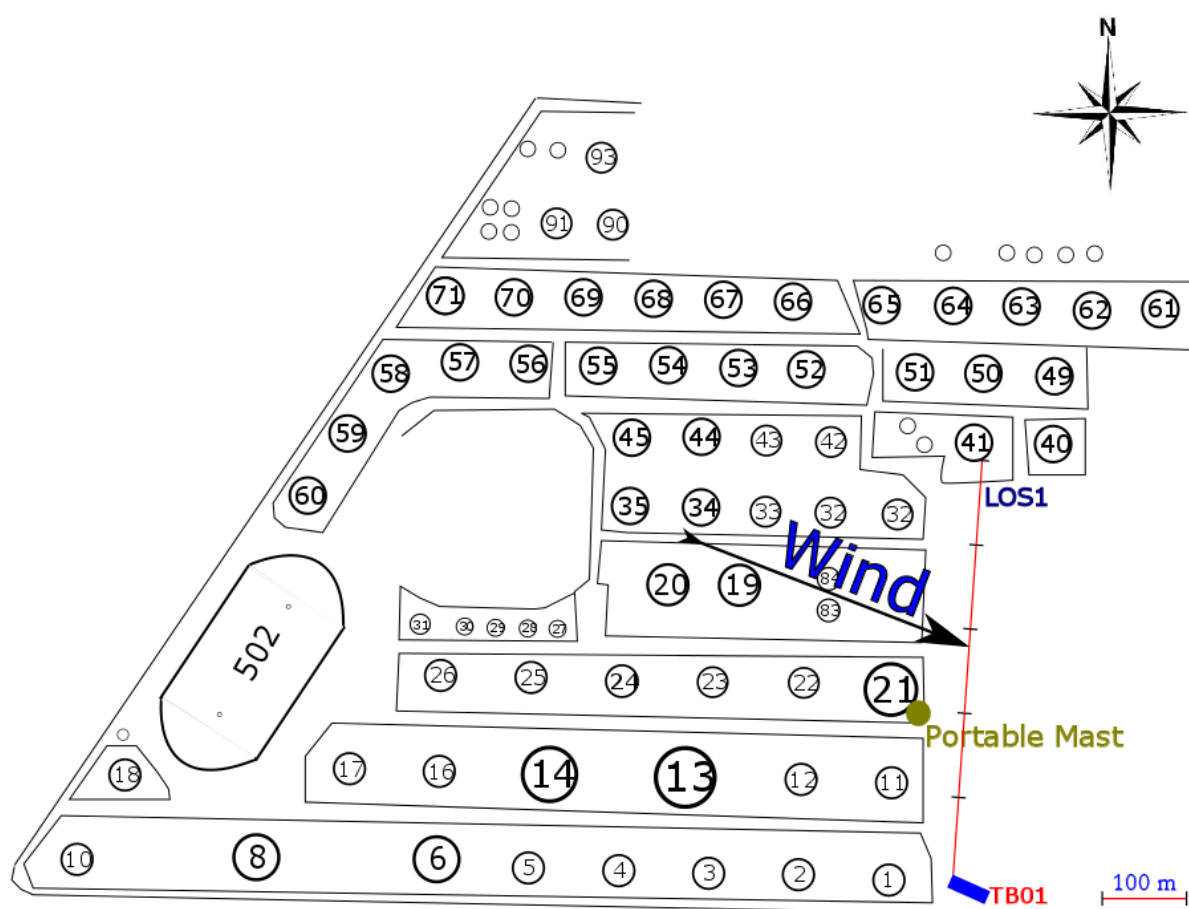
The lines-of-sight (LOS) used at each measurement location are shown in Figures 4.1 through 4.16. The figures also show the average wind direction measured over the full time frame during which the measurements from a given location took place. The DIAL maximum scan range is dependent on the atmospheric conditions, and therefore varies from day to day and it can also change during the same day.

Figures designated a1 and a2 are exemplar contour plots and visualizations of the emissions observed in the downwind DIAL measurements. The contour plots (a1 figures) are scaled to the maximum concentration value in each plot while all the 3D visualizations (a2 figures) use a common colour scale (shown below the first scan result in Figure 2.1a2), which was up to a maximum of 0.1 ppm for benzene and 5.0 ppm for VOC. Therefore, the colour scale of the contour plot is different with respect to the colour scale of the 3D visualization. In some cases this difference in scaling leads to a slight difference in apparent plume shapes between a contour plot and the 3D visualization.

Tables 4.1 to 4.16 report the emission rates determined for each scan made during the measurement campaign. The scan numbers are not necessarily sequential because they exclude scans recorded for data quality checks and scans aborted by the operator. No valid scan has been eliminated from the report. The tables also list the locations and the LOS used for each measurement. Negative emission rate values can occur because of the random noise on a small signal and these are reported in the tables. However, in the summary Tables 5.1 and 6.1 non-physical negative results are reported as zero. The wind directions reported in the tables are from the sensor used for the emission rate calculations. The wind speeds reported in the tables are from the higher of the sensors used to determine the wind profile. The notes in each table are only indicative of the area measured in a specific LOS to aid the reader in visualising the general location from where the plumes are coming. Reference should be made to the results discussion (Sections 5 and 6) for more detailed explanations.

Table 4.1 Benzene Emission rate determined from TB01 on 28th of September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
1	TB01/LOS1	14:50	15:01	6.1	292.8	0.46	Downwind Tanks 11,21,22,23,24,19,20,83
2	TB01/LOS1	15:02	15:13	6.2	284.8	0.46	Downwind Tanks 11,21,22,23,24,19,20,83
3	TB01/LOS1	15:13	15:24	6.3	315.6	0.59	Downwind Tanks 11,21,22,23,24,19,20,83
4	TB01/LOS1	15:24	15:35	5.3	286.9	0.32	Downwind Tanks 11,21,22,23,24,19,20,83
6	TB01/LOS1	15:40	15:51	5.6	286.3	1.07	Downwind Tanks 11,21,22,23,24,19,20,83

**Figure 4.1 Measurement configuration for location TB01 on 28th of September.**

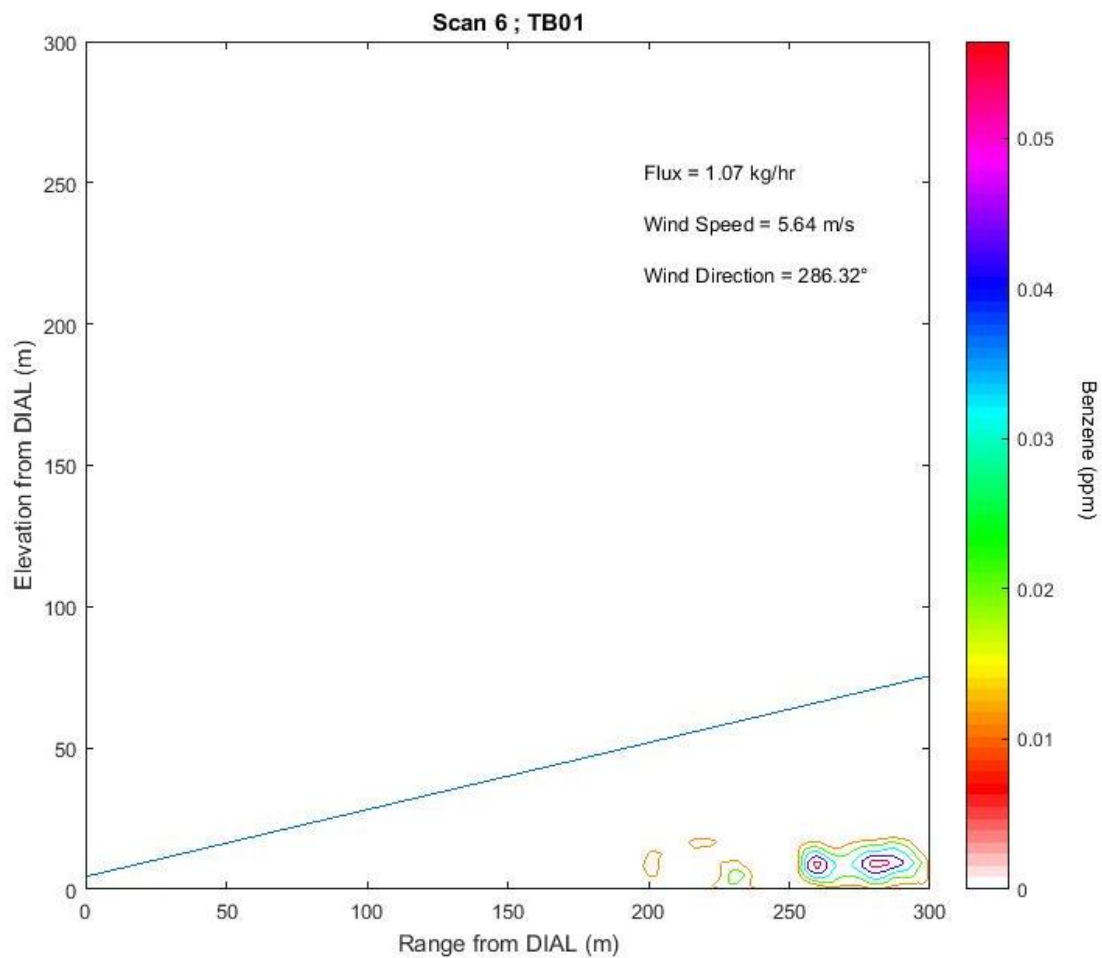


Figure 4.1a1 Observed benzene concentration for Scan 6 representing TB01/LOS1.

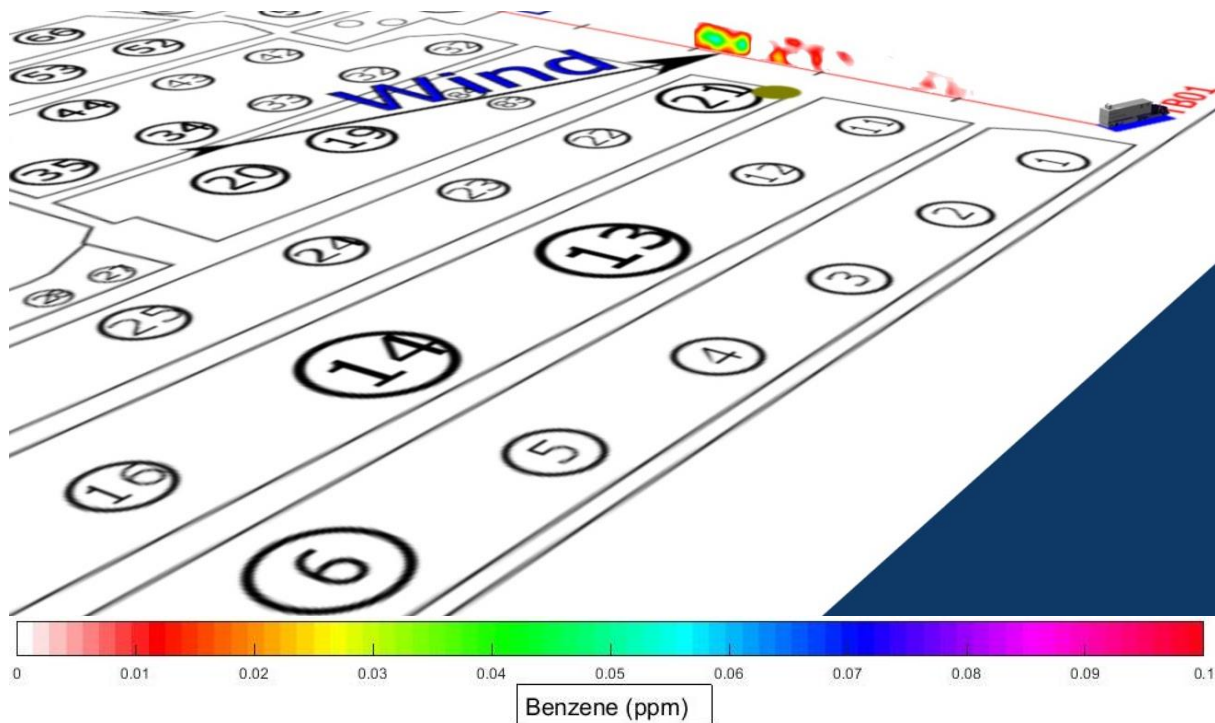


Figure 4.1a2 Visualisation of emission rate for Scan 6 representing TB01/LOS1.

Table 4.2 Benzene Emission rate determined from TB02 on 29th of September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
7	TB02/LOS1	09:20	09:32	0.8	124.5	0.10	Downwind Tanks 90,91,93
8	TB02/LOS1	09:32	09:44	0.3	203.6	-	Wind Speed Too Low
9	TB02/LOS1	09:44	09:56	0.5	239.4	0.02	Downwind NW Corner Small Tanks & 71
10	TB02/LOS1	09:56	10:08	0.9	260.5	0.07	Downwind NW Corner Small Tanks & 71
11	TB02/LOS1	10:09	10:20	0.6	187.3	0.03	Downwind Tanks 91,70

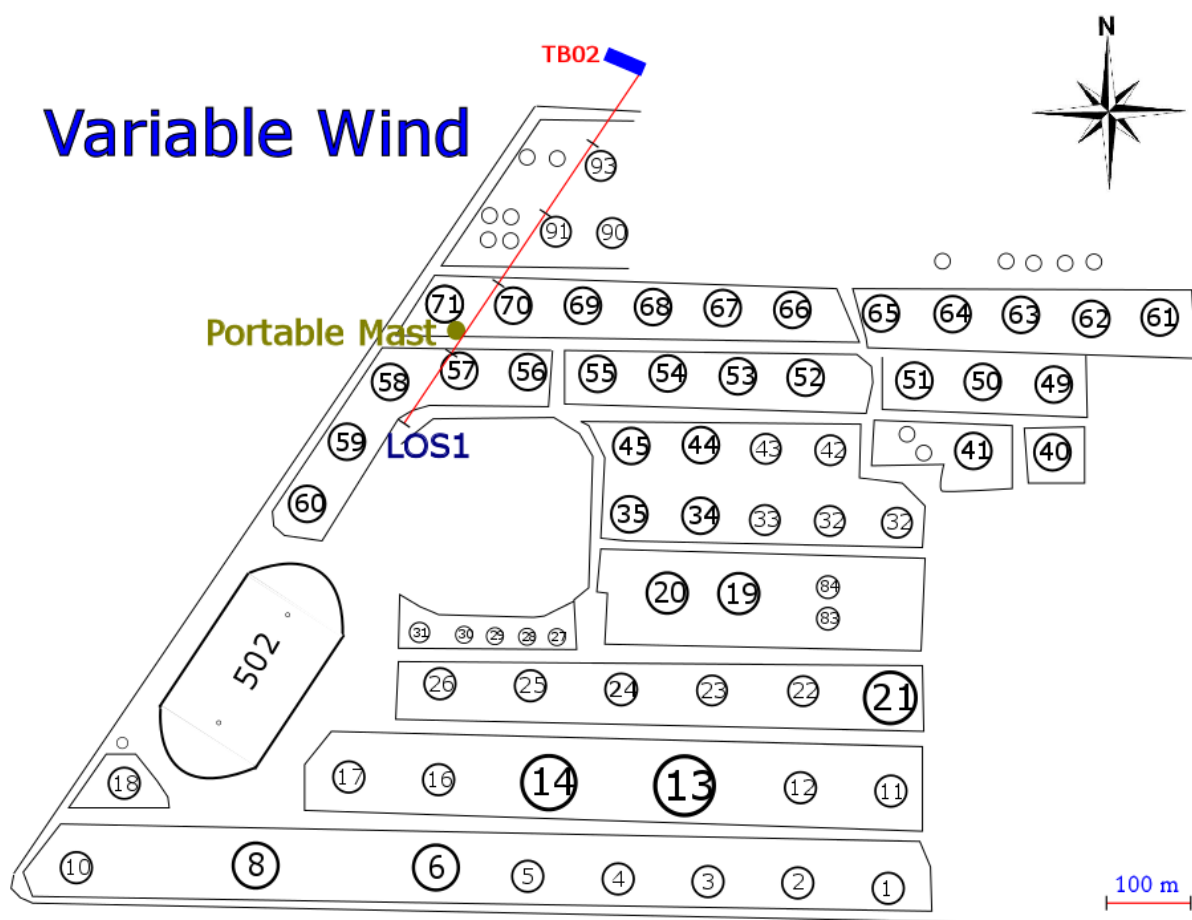
Figure 4.2 Measurement configuration for location TB02 on 29th of September.

Table 4.3 Benzene Emission rate determined from TB03 on 29th of September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
13	TB03/LOS1	11:39	11:51	2.6	272.1	0.14	Downwind Tanks 33,34,35,43,44,45
14	TB03/LOS1	11:51	12:03	3.0	205.9	-	Wind Direction Almost Parallel to LOS
15	TB03/LOS1	12:04	12:16	2.4	217.6	0.08	Downwind Tanks 33,34,43,20
16	TB03/LOS1	12:16	12:28	2.1	172.1	0.05	Downwind Tanks 83,84,32,42
17	TB03/LOS1	12:28	12:40	2.5	214.6	0.09	Downwind Tanks 33,34,43,20

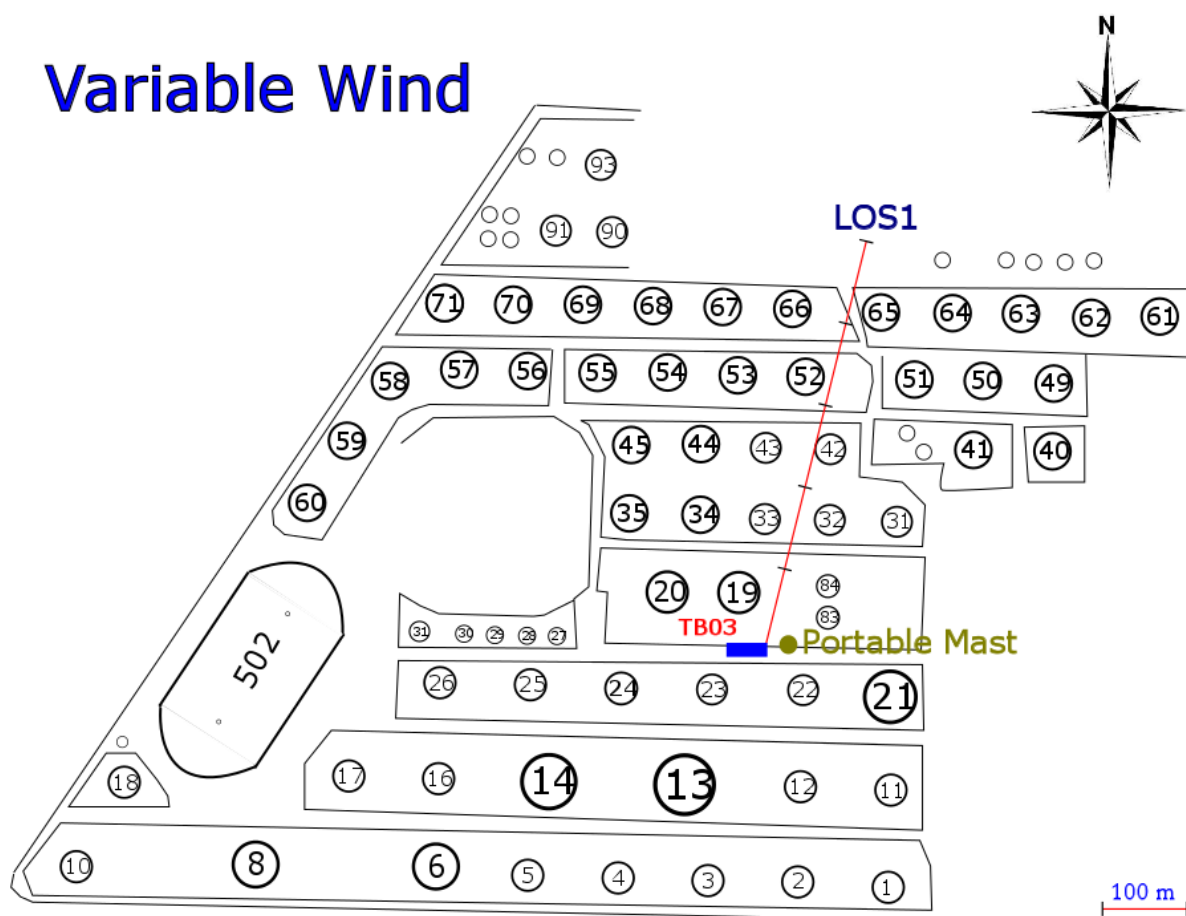
**Figure 4.3 Measurement configuration for location TB03 on 29th of September.**

Table 4.4 Benzene Emission rate determined from TB04 on 29th of September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
18	TB04/LOS1	13:24	13:36	2.0	93.7	-0.03	Downwind Tanks 14,13,12,11,5,4,3,2,1
19	TB04/LOS1	13:36	13:48	1.5	114.8	0.02	Downwind Tanks 14,13,12,11,5,4,3,2,1
20	TB04/LOS1	13:48	14:01	0.7	239.6	-0.01	Downwind Tanks 6,16
21	TB04/LOS1	14:01	14:13	5.0	313.7	0.24	Tanks 26,16,17 & Central Area 502
22	TB04/LOS1	14:13	14:25	5.5	301.8	0.17	Tanks 26,16,17 & Central Area 502
23	TB04/LOS1	14:25	14:37	5.3	297.4	0.21	Tanks 26,16,17 & Central Area 502
24	TB04/LOS1	14:37	14:49	5.3	310.4	0.17	Tanks 26,16,17 & Central Area 502

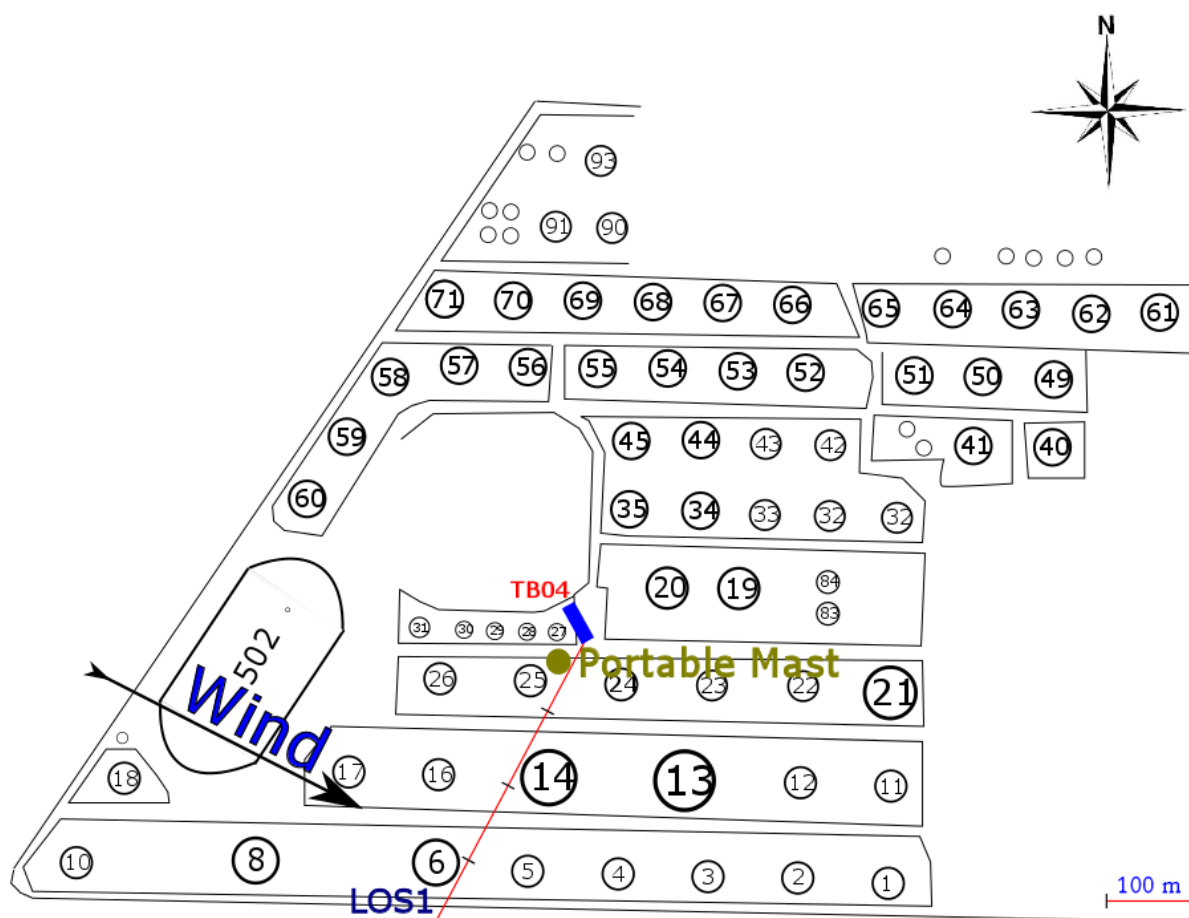
Figure 4.4 Measurement configuration for location TB04 on 29th of September.

Table 4.5 Benzene Emission rate determined from TB05 on 29th of September.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
26	TB05/LOS1	15:35	15:46	5.5	311.2	0.39	Tanks 42,52,66,53,67,54,68,69
27	TB05/LOS1	15:46	15:57	6.1	304.2	0.06	Tanks 42,52,66,53,67,54,68,69
28	TB05/LOS1	15:57	16:08	5.1	308.8	0.21	Tanks 42,52,66,53,67,54,68,69
29	TB05/LOS1	16:08	16:20	5.1	301.0	0.17	Tanks 42,52,66,53,67,54,68,69

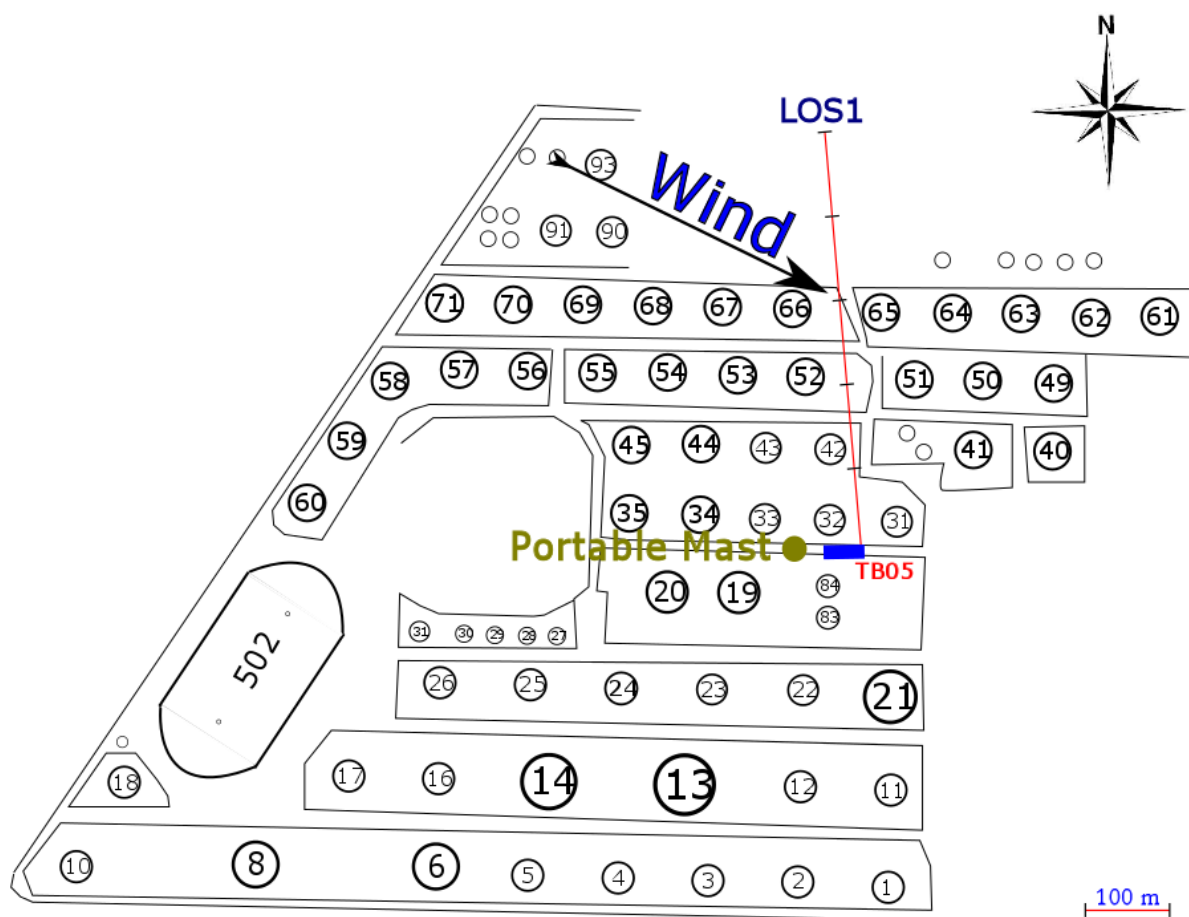
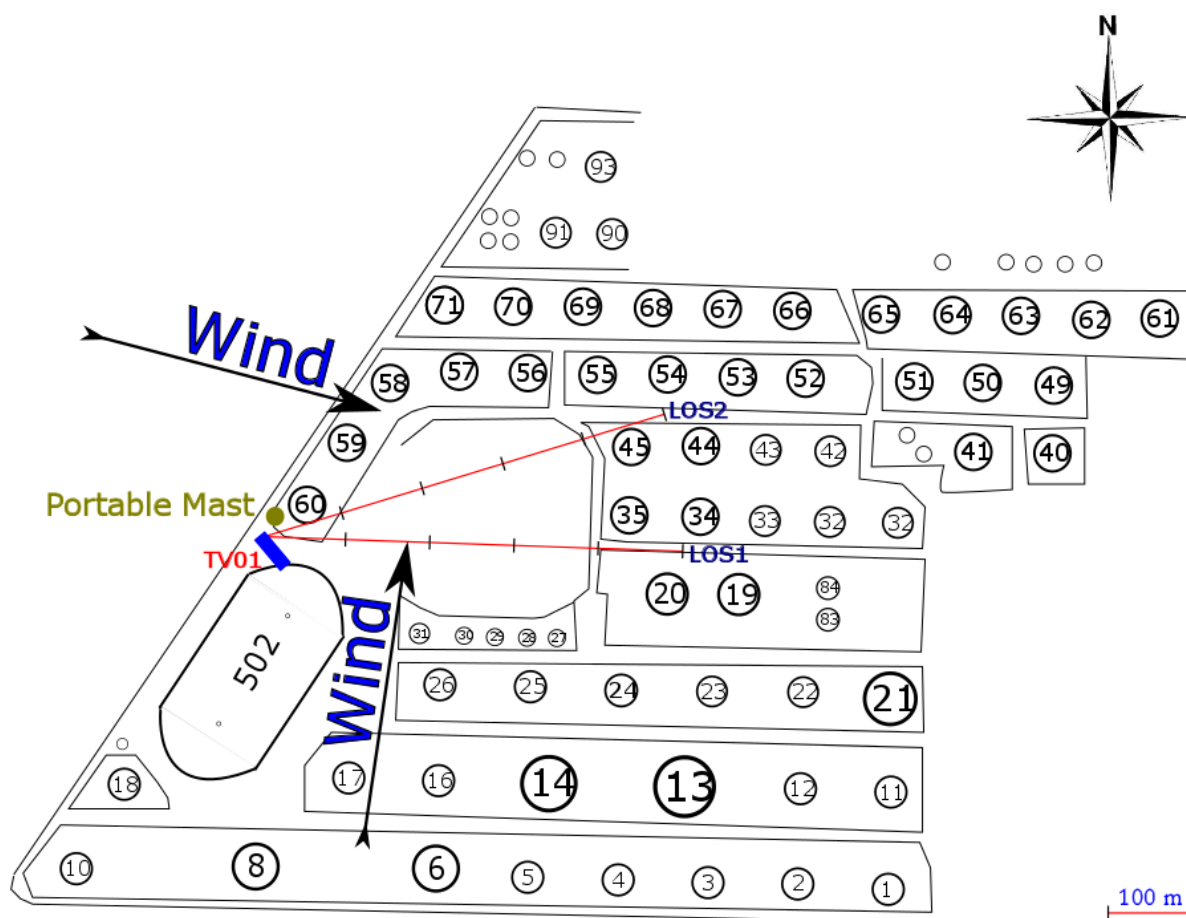
**Figure 4.5 Measurement configuration for location TB05 on 29th of September.**

Table 4.6 VOC Emission rate determined from TV01 on 1st of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
30	TV01/LOS1	14:04	14:13	2.5	178.9	15.47	Downwind Tanks 29,30,31,26,16,17,6
31	TV01/LOS1	14:13	14:22	1.7	197.8	11.25	Downwind Tanks 29,30,31,26,16,17,6
32	TV01/LOS2	14:37	14:45	4.3	290.1	7.93	Downwind Tanks 58 & 59
33	TV01/LOS2	14:45	14:54	4.4	287.0	6.36	Downwind Tanks 58 & 59
34	TV01/LOS2	14:54	15:03	5.2	277.2	7.59	Downwind Tanks 58 & 59

Figure 4.6 Measurement configuration for location TV01 on 1st of October.

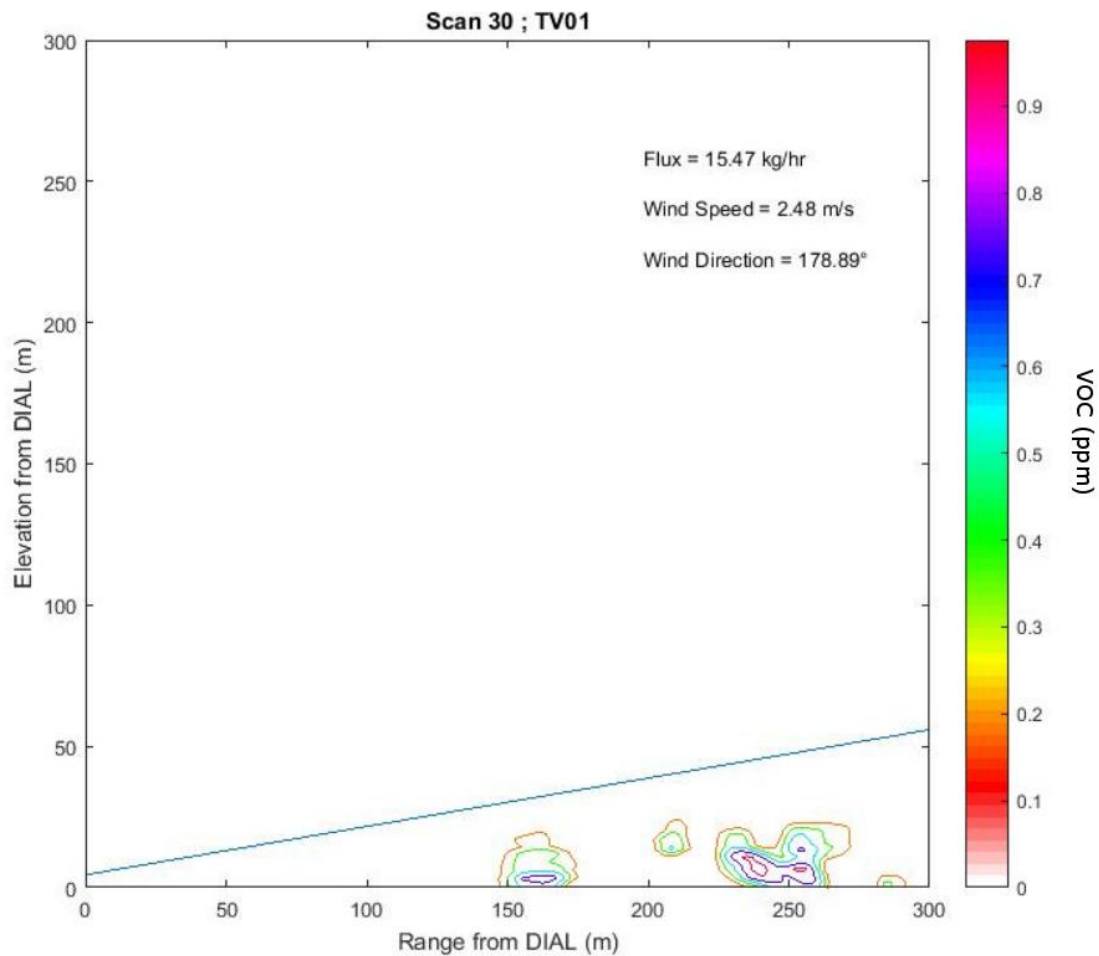


Figure 4.6a1 Observed VOC concentration for Scan 30 representing TV01/LOS1.

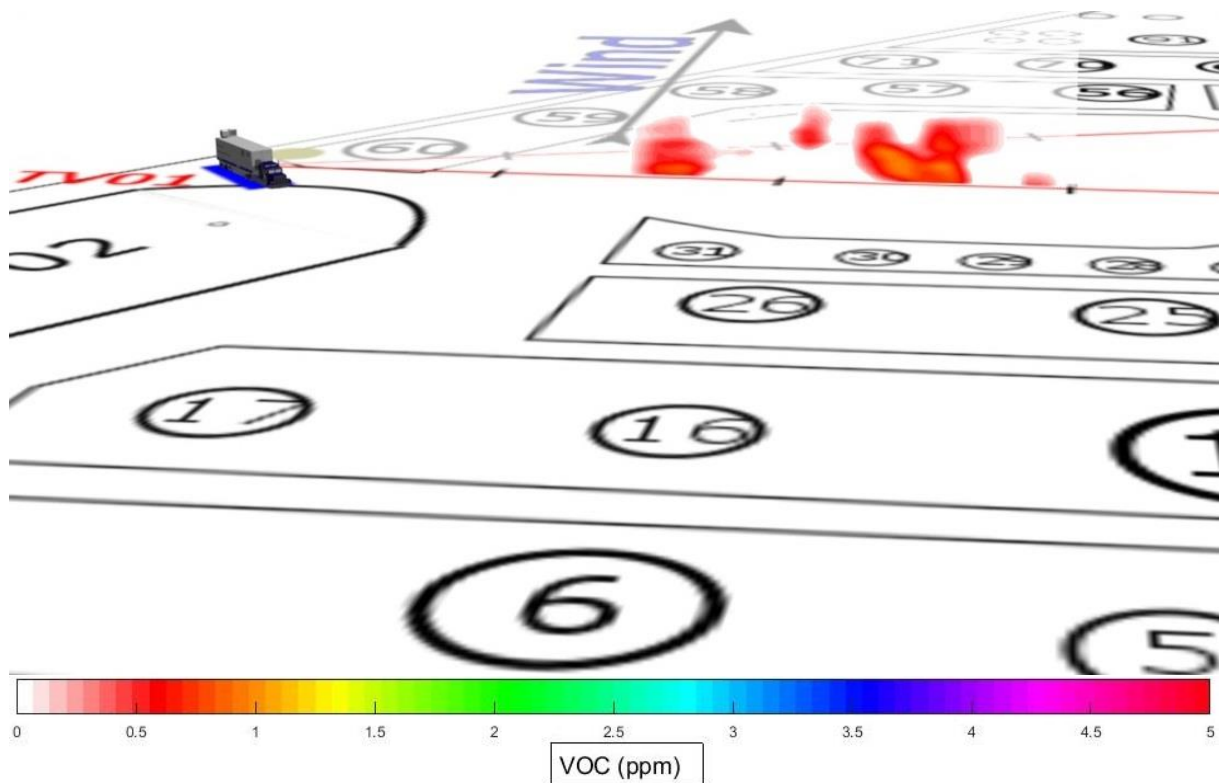


Figure 4.6a2 Visualisation of emission rate for Scan 30 representing TV01/LOS1.

Table 4.7 VOC Emission rate determined from TV02 on 1st of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
36	TV02/LOS1	15:51	15:59	5.1	287.4	55.88	Downwind Reservoir 502 & Tank 17
37	TV02/LOS1	15:59	16:06	5.3	286.3	57.66	Downwind Reservoir 502 & Tank 17
38	TV02/LOS1	16:07	16:14	4.9	284.3	66.75	Downwind Reservoir 502 & Tank 17
39	TV02/LOS1	16:14	16:22	4.6	300.1	67.04	Downwind Reservoir 502 & Tank 17

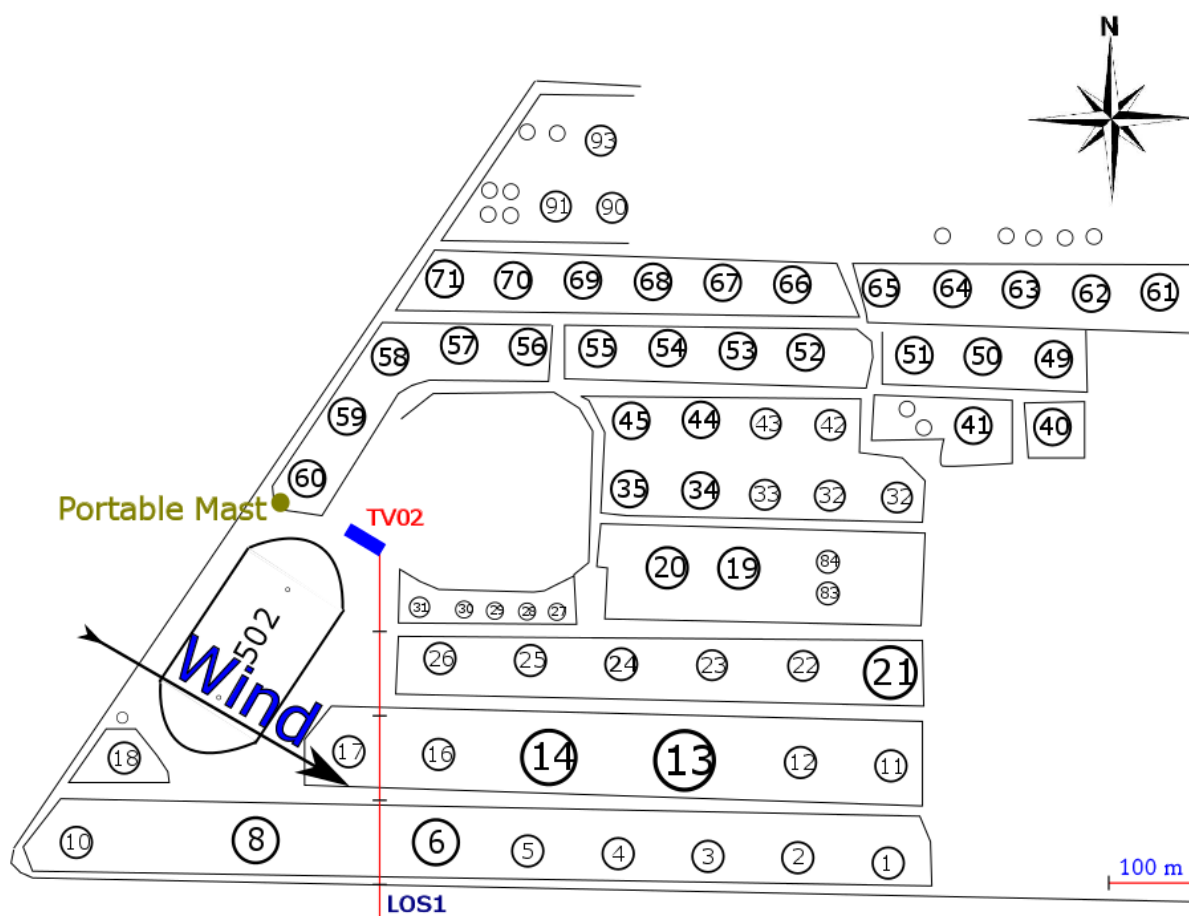
**Figure 4.7 Measurement configuration for location TV02 on 1st of October.**

Table 4.8 VOC Emission rate determined from TV03 on 2nd of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
43	TV03/LOS1	10:38	10:46	1.1	143.3	1.52	Downwind Tanks 3 & 4
44	TV03/LOS1	10:46	10:55	1.2	178.7	-	Wind Direction Almost Parallel to LOS
45	TV03/LOS1	10:56	11:05	1.3	223.8	1.98	Downwind Tanks 5 & 14
46	TV03/LOS2	11:07	11:18	0.9	190.7	2.86	Downwind Tanks 26,16,17,6
47	TV03/LOS2	11:18	11:28	1.9	190.1	4.75	Downwind Tanks 26,16,17,6
48	TV03/LOS2	11:29	11:40	3.2	190.8	3.87	Downwind Tanks 26,16,17,6
49	TV03/LOS2	11:40	11:51	2.1	197.4	3.86	Downwind Tanks 26,16,17,6
50	TV03/LOS3	11:55	12:06	1.2	200.0	8.17	Downwind Tanks 23,22,13,4,3
51	TV03/LOS3	12:06	12:17	2.3	199.2	11.12	Downwind Tanks 23,22,13,4,3
52	TV03/LOS3	12:18	12:29	3.3	201.7	9.21	Downwind Tanks 23,22,13,4,3
53	TV03/LOS3	12:29	12:40	3.5	199.9	9.26	Downwind Tanks 23,22,13,4,3

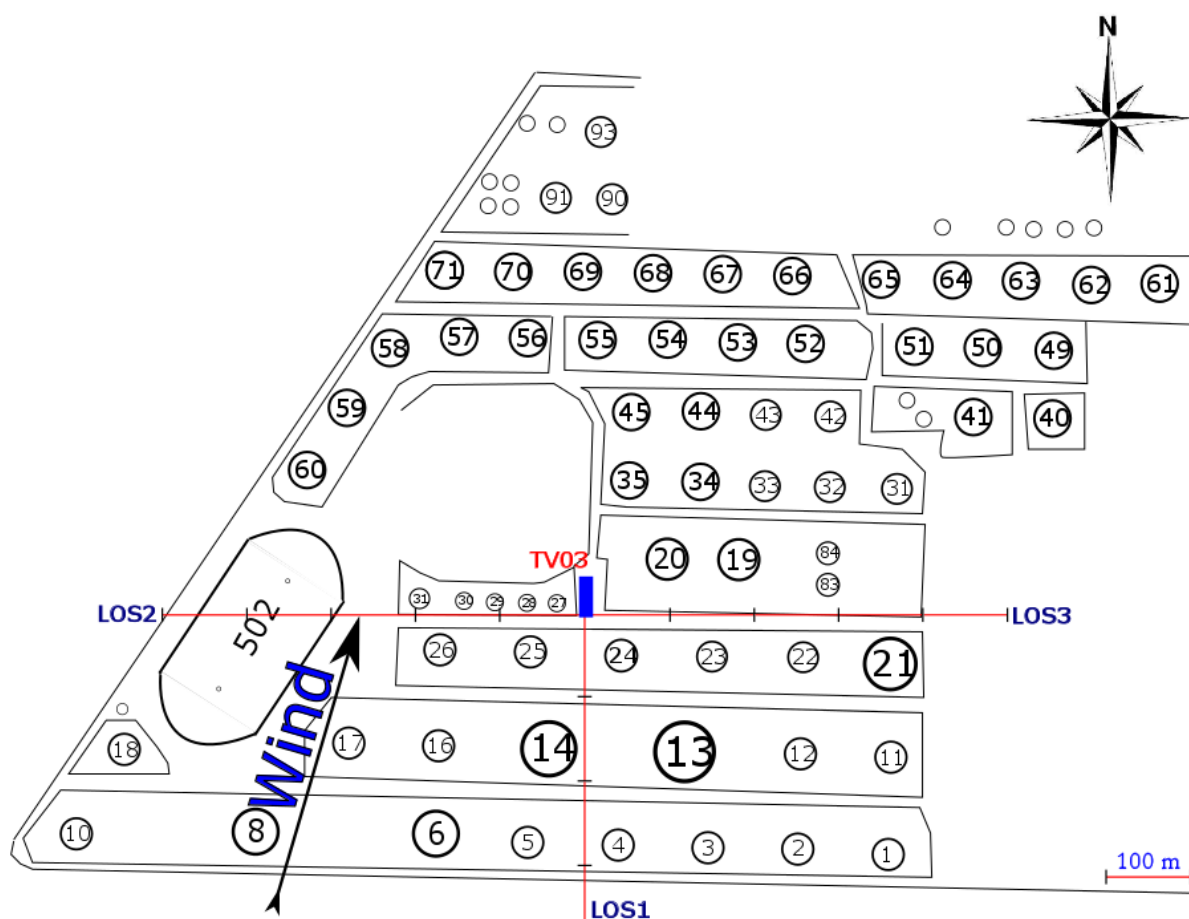
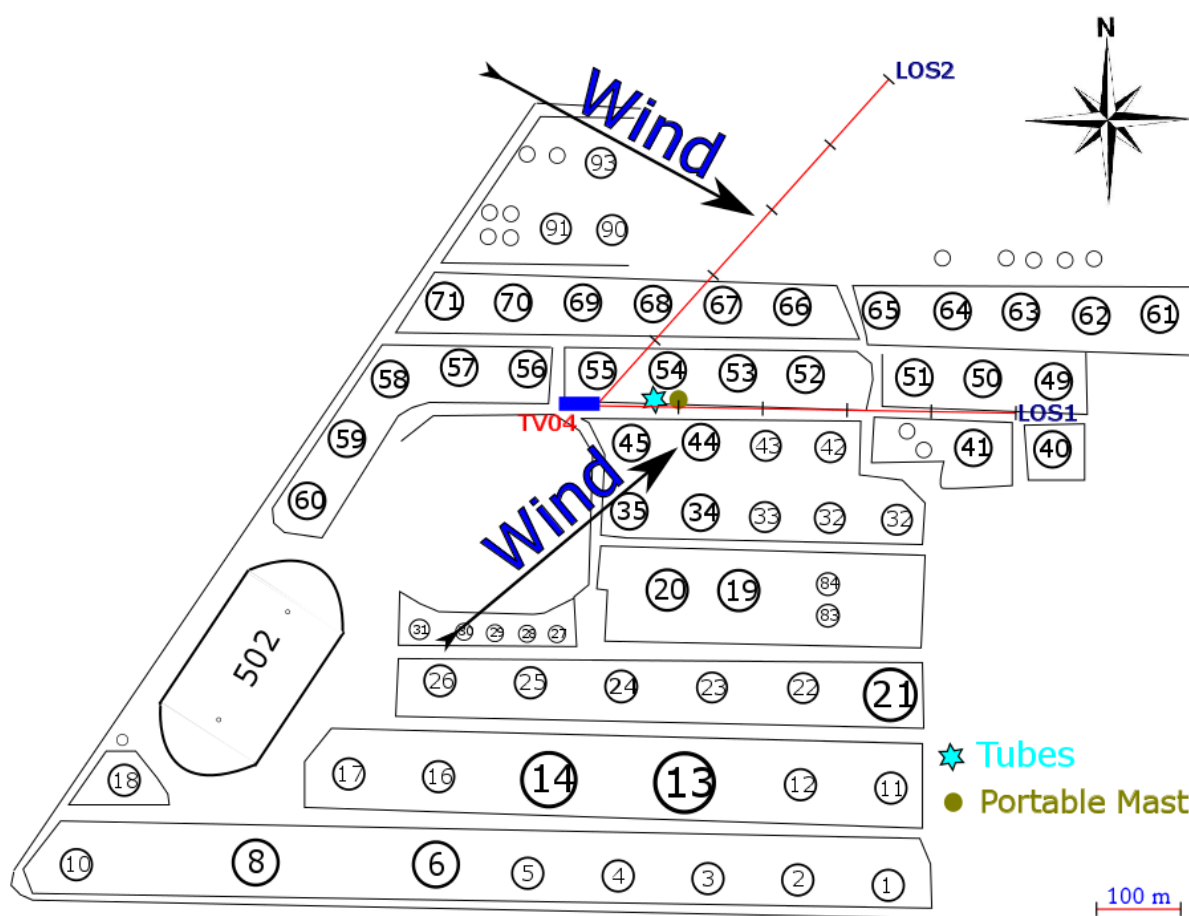
**Figure 4.8 Measurement configuration for location TV03 on 2nd of October.**

Table 4.9 VOC Emission rate determined from TV04 on 2nd of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
55	TV04/LOS1	13:24	13:34	2.2	206.6	15.56	Tanks 44,43,34,33,20,19
56	TV04/LOS1	13:35	13:45	3.3	254.9	4.70	Tanks 45,44,43,35
57	TV04/LOS2	13:50	14:00	5.0	300.6	27.48	Tanks 68,69,90,91,93 + Small Tanks
58	TV04/LOS2	14:00	14:11	5.1	298.2	29.06	Tanks 68,69,90,91,93 + Small Tanks
59	TV04/LOS2	14:11	14:21	4.7	300.9	28.99	Tanks 68,69,90,91,93 + Small Tanks
60	TV04/LOS2	14:21	14:32	4.9	293.9	26.76	Tanks 68,69,90,91,93 + Small Tanks

**Figure 4.9 Measurement configuration for location TV04 on 2nd of October.**

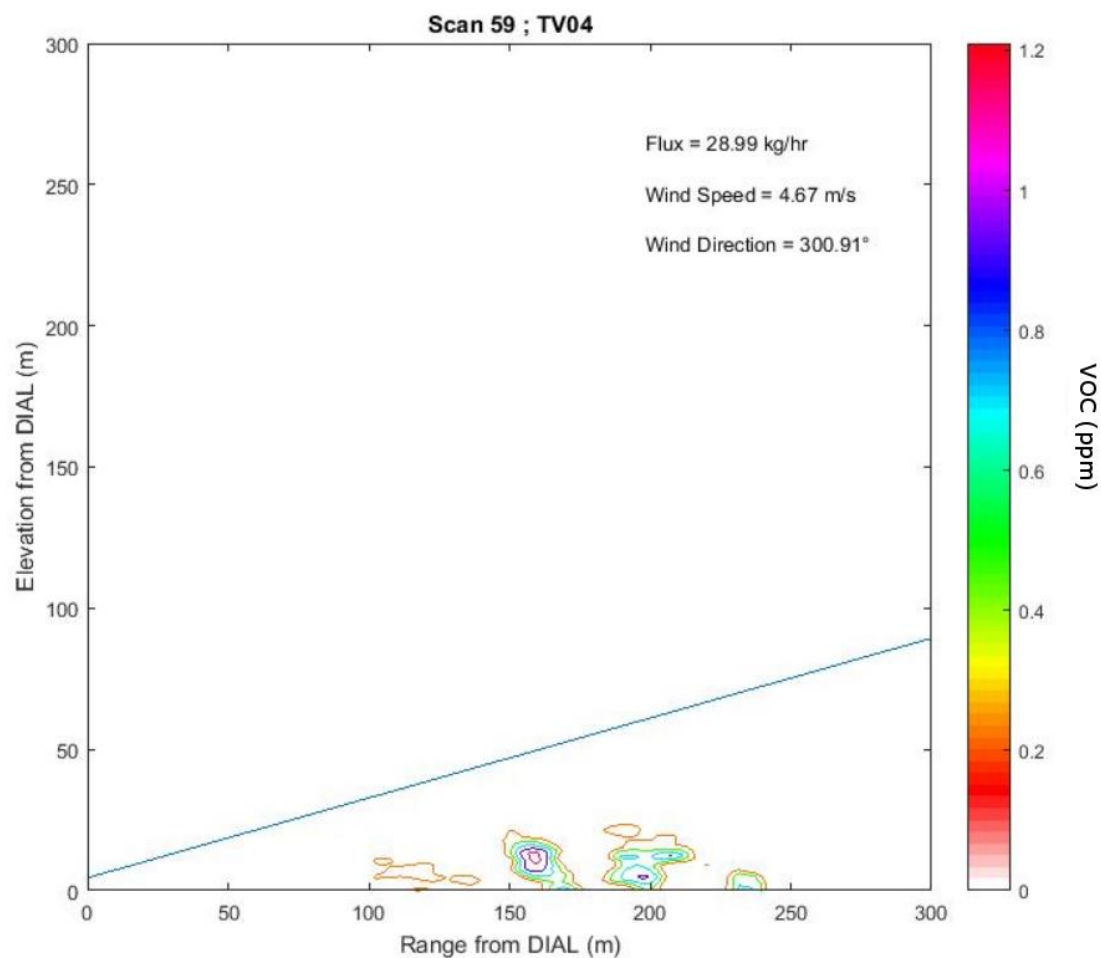


Figure 4.9a1 Observed VOC concentration for Scan 59 representing TV04/LOS2.

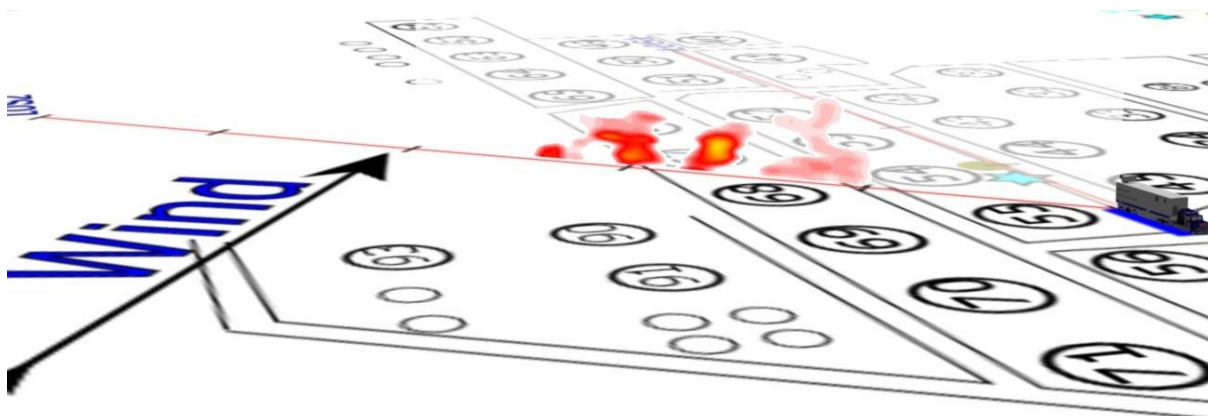


Figure 4.9a2 Visualisation of emission rate for Scan 59 representing TV04/LOS2.

Table 4.10 VOC Emission rate determined from TV05 on 2nd of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
61	TV05/LOS1	15:05	15:14	6.0	277.5	18.10	Tanks 53,54,55,56,57,58,43,44,45
62	TV05/LOS1	15:15	15:34	6.1	283.5	17.68	Tanks 53,54,55,56,57,58,43,44,45
63	TV05/LOS1	15:34	15:52	6.0	276.6	28.15	Tanks 53,54,55,56,57,58,43,44,45
64	TV05/LOS1	15:52	16:11	5.7	277.2	18.83	Tanks 53,54,55,56,57,58,43,44,45

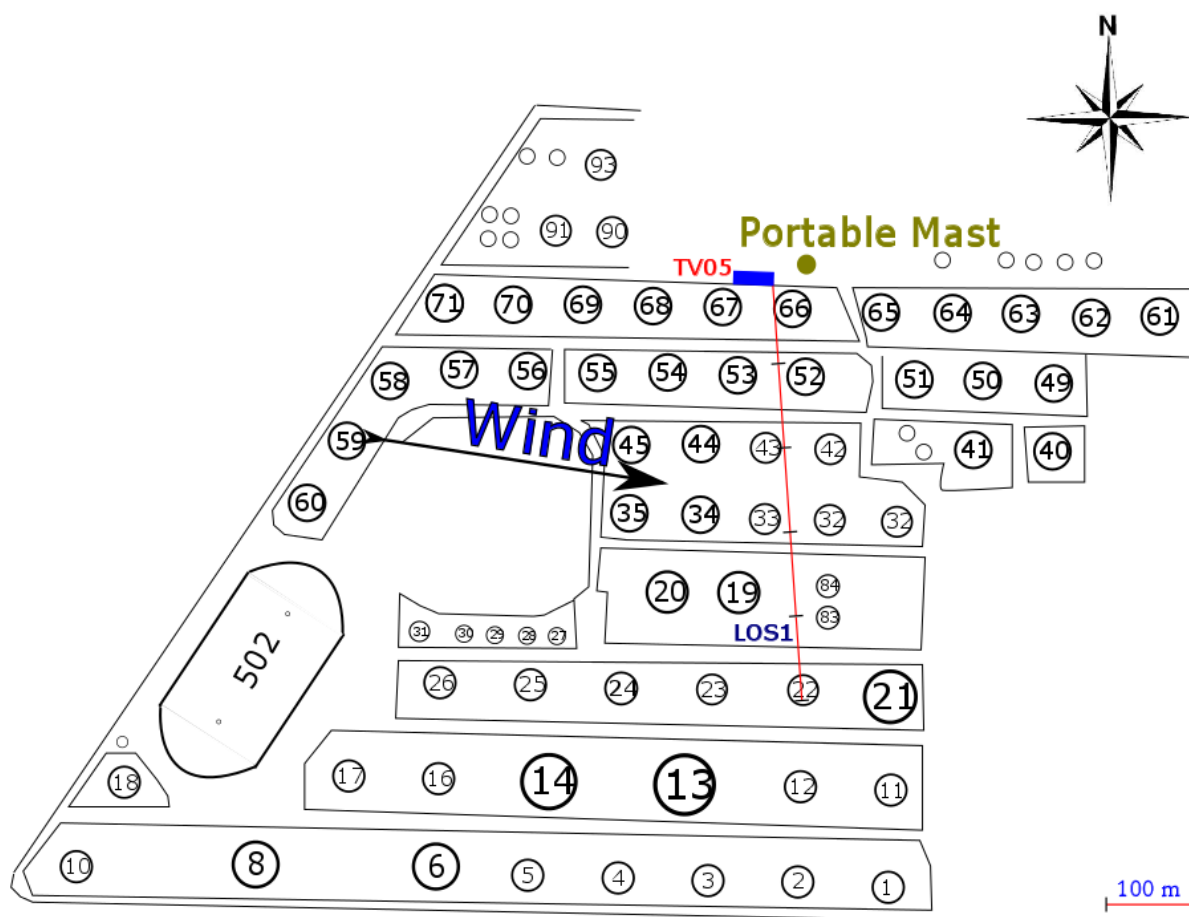
**Figure 4.10 Measurement configuration for location TV05 on 2nd of October.**

Table 4.11 VOC Emission rate determined from TV06 on 5th of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
65	TV06/LOS1	11:04	11:13	2.2	135.7	18.72	Downwind Tanks 23,22,12,11,1
66	TV06/LOS1	11:13	11:22	1.7	130.8	16.09	Downwind Tanks 23,22,12,11,1
67	TV06/LOS1	11:22	11:30	2.9	131.2	24.41	Downwind Tanks 23,22,12,11,1
68	TV06/LOS1	11:31	11:40	3.0	140.8	26.30	Downwind Tanks 23,22,12,11,1
69	TV06/LOS2	11:48	11:57	3.5	156.8	3.88	Downwind Tanks 14,5,4
70	TV06/LOS3	12:02	12:13	2.7	170.5	266.39	Downwind Tanks 16,6
71	TV06/LOS3	12:14	12:25	3.5	196.0	254.20	Downwind Tanks 16,6
72	TV06/LOS3	12:25	12:35	4.5	198.5	305.57	Downwind Tanks 16,6
73	TV06/LOS3	12:36	12:46	4.4	188.3	297.35	Downwind Tanks 16,6
74	TV06/LOS4	12:50	13:00	3.8	193.7	264.32	Downwind Tanks 16,6,26,17
75	TV06/LOS4	13:00	13:11	4.5	185.6	292.04	Downwind Tanks 16,6,26,17
76	TV06/LOS4	13:11	13:21	4.4	193.7	269.81	Downwind Tanks 16,6,26,17
77	TV06/LOS4	13:21	13:32	4.4	189.3	258.57	Downwind Tanks 16,6,26,17
78	TV06/LOS5	13:39	13:48	4.0	191.9	24.02	Downwind Tanks 13,12,3,2
79	TV06/LOS5	13:48	13:57	4.9	166.1	19.32	Downwind Tanks 13,12,3,2
80	TV06/LOS5	13:57	14:05	4.9	192.8	16.91	Downwind Tanks 13,12,3,2
81	TV06/LOS5	14:06	14:14	5.2	184.1	22.88	Downwind Tanks 13,12,3,2

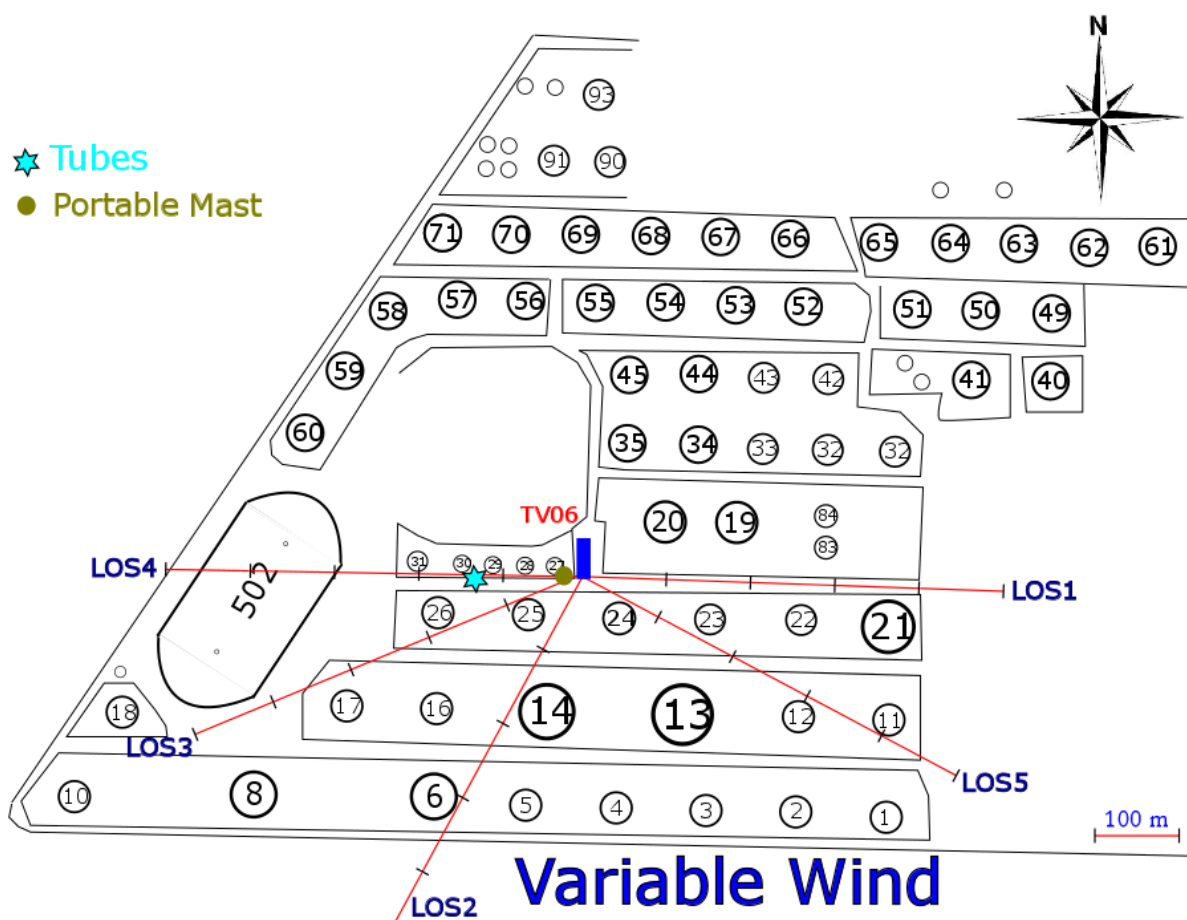
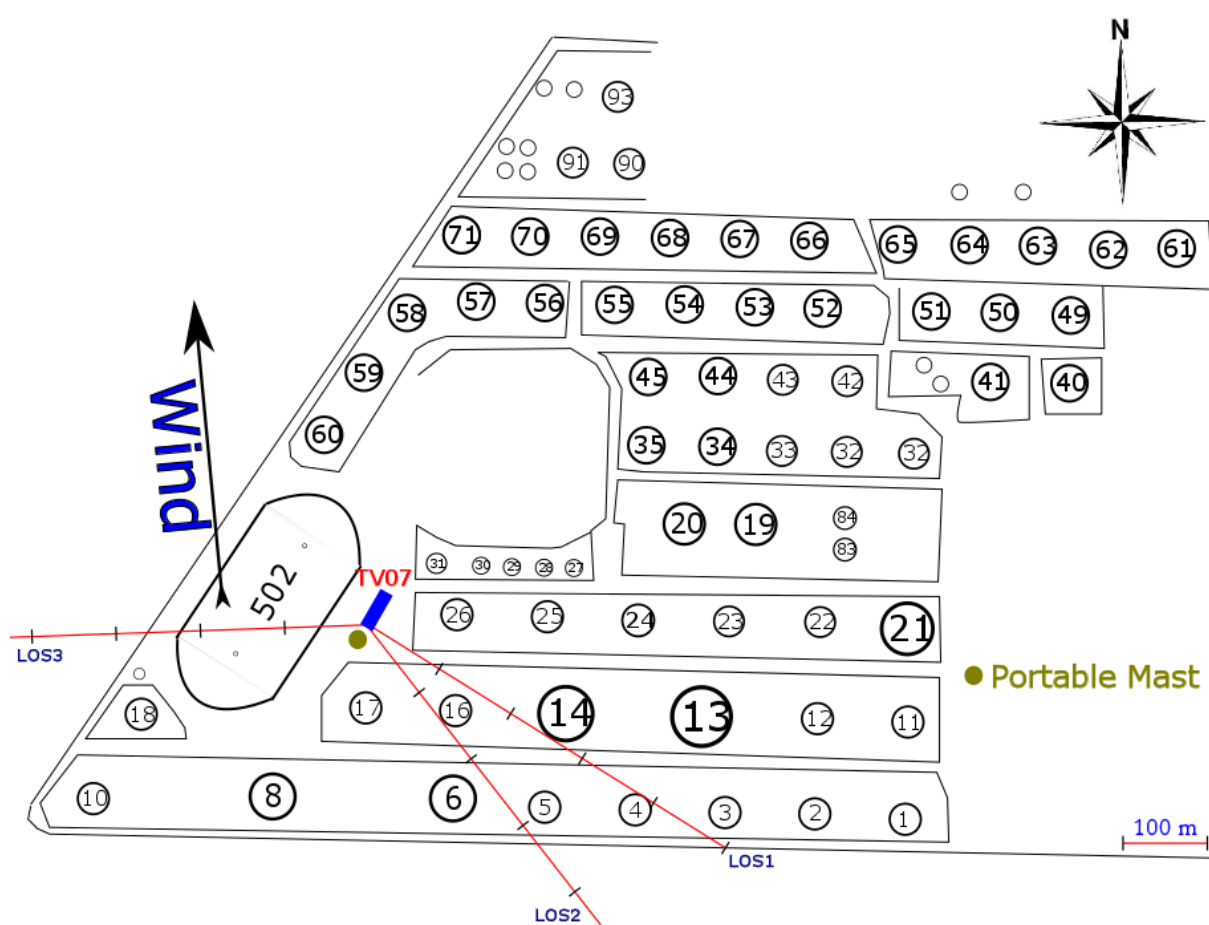
**Figure 4.11 Measurement configuration for location TV06 on 5th of October.**

Table 4.12 VOC Emission rate determined from TV07 on 5th of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
83	TV07/LOS1	14:53	15:02	4.6	181.8	398.63	Downwind Tanks 16,6,5
84	TV07/LOS1	15:02	15:12	4.6	167.2	250.36	Downwind Tanks 16,6,5
85	TV07/LOS1	15:15	15:24	4.9	183.1	271.43	Downwind Tanks 16,6,5
86	TV07/LOS1	15:26	15:36	5.1	171.9	240.81	Downwind Tanks 16,6,5
87	TV07/LOS2	15:41	15:50	4.1	170.9	2.18	Downwind Tank 6
88	TV07/LOS3	15:55	16:04	3.8	183.8	41.71	Downwind Reservoir 502 South Vent
89	TV07/LOS3	16:05	16:13	4.0	160.8	47.82	Downwind Reservoir 502 South Vent
90	TV07/LOS3	16:13	16:20	3.6	146.1	34.14	Downwind Reservoir 502 South Vent

**Figure 4.12 Measurement configuration for location TV07 on 5th of October.**

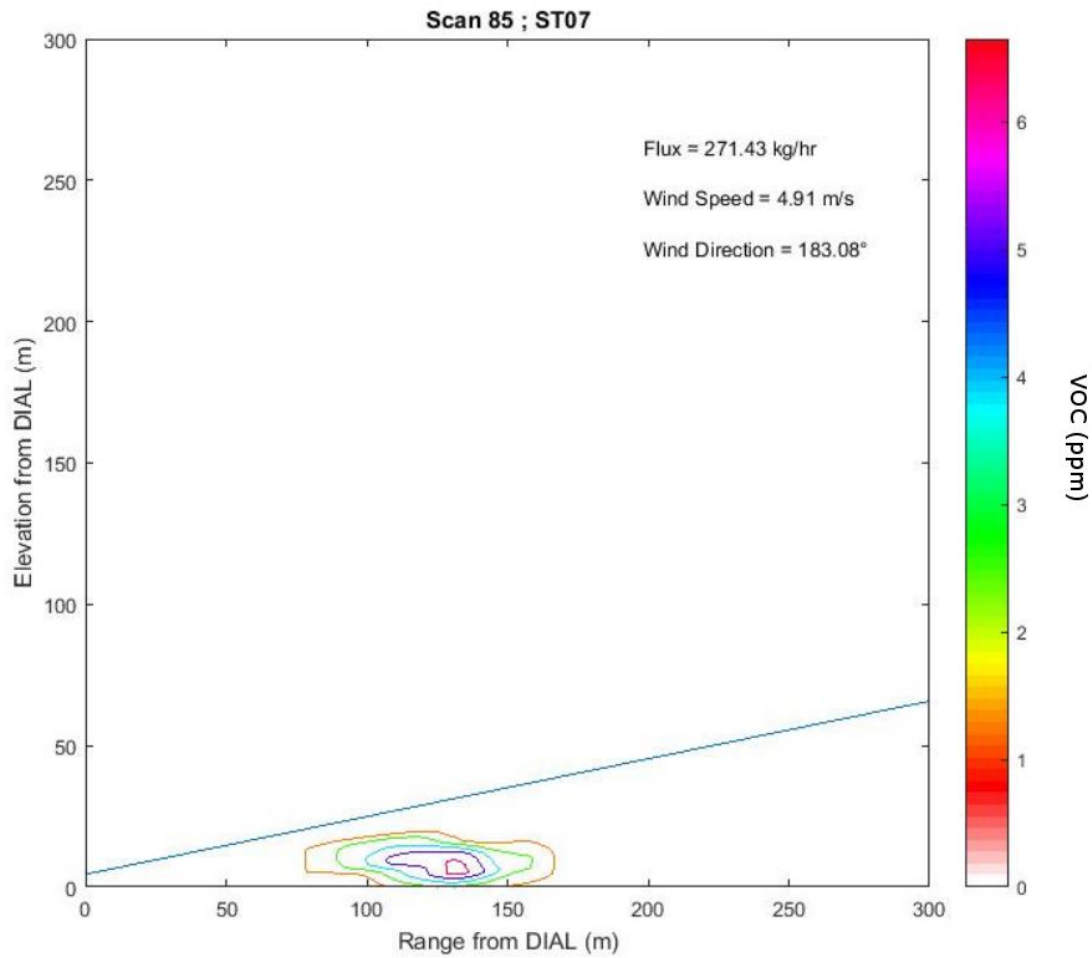


Figure 4.12a1 Observed VOC concentration for Scan 85 representing TV07/LOS1.

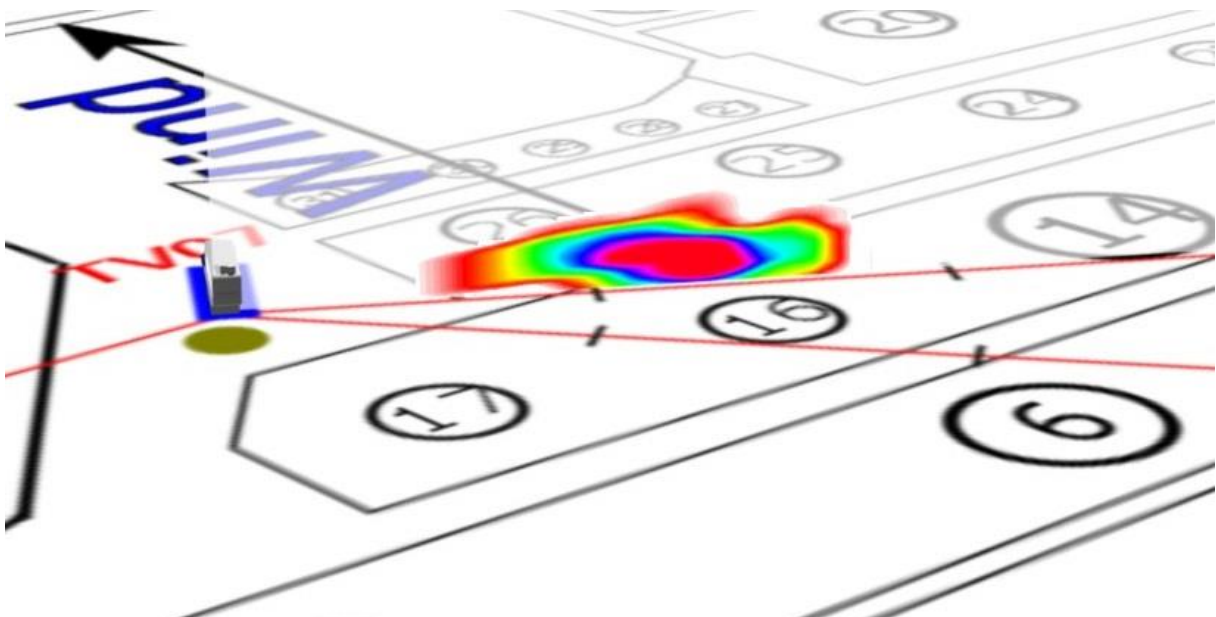


Figure 4.12a2 Visualisation of emission rate for Scan 85 representing TV07/LOS1.

Table 4.13 VOC Emission rate determined from TV08 on 6th of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
91	TV08/LOS1	11:21	11:28	3.0	294.5	36.69	Downwind Reservoir 502 South Vent
92	TV08/LOS1	11:29	11:35	4.3	278.4	-	Wind Direction Almost Parallel to LOS
93	TV08/LOS1	11:36	11:42	4.1	276.1	-	Wind Direction Almost Parallel to LOS
94	TV08/LOS1	11:45	11:52	3.7	300.2	32.80	Downwind Reservoir 502 South Vent
95	TV08/LOS2	11:58	12:09	3.5	289.5	3.86	Downwind Reservoir 502 North Vent
96	TV08/LOS2	12:10	12:17	3.7	271.1	1.65	Downwind Reservoir 502 North Vent
97	TV08/LOS2	12:17	12:24	3.0	277.7	1.92	Downwind Reservoir 502 North Vent
98	TV08/LOS2	12:24	12:31	2.6	265.3	1.96	Downwind Reservoir 502 North Vent
99	TV08/LOS2	12:48	12:56	4.4	277.7	2.39	Downwind Reservoir 502 North Vent
100	TV08/LOS2	12:57	13:05	3.9	287.6	3.74	Downwind Reservoir 502 North Vent
101	TV08/LOS2	13:05	13:13	3.6	284.5	3.26	Downwind Reservoir 502 North Vent

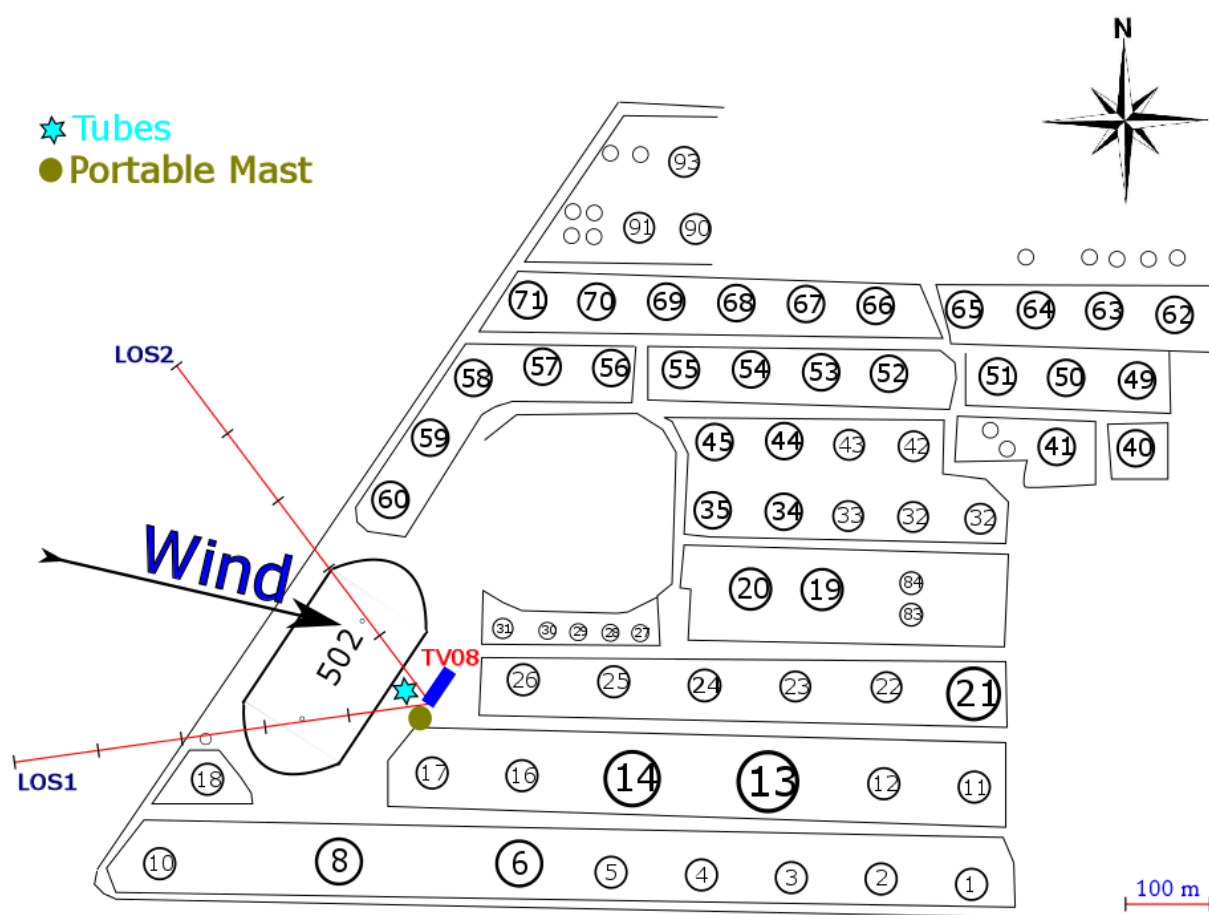
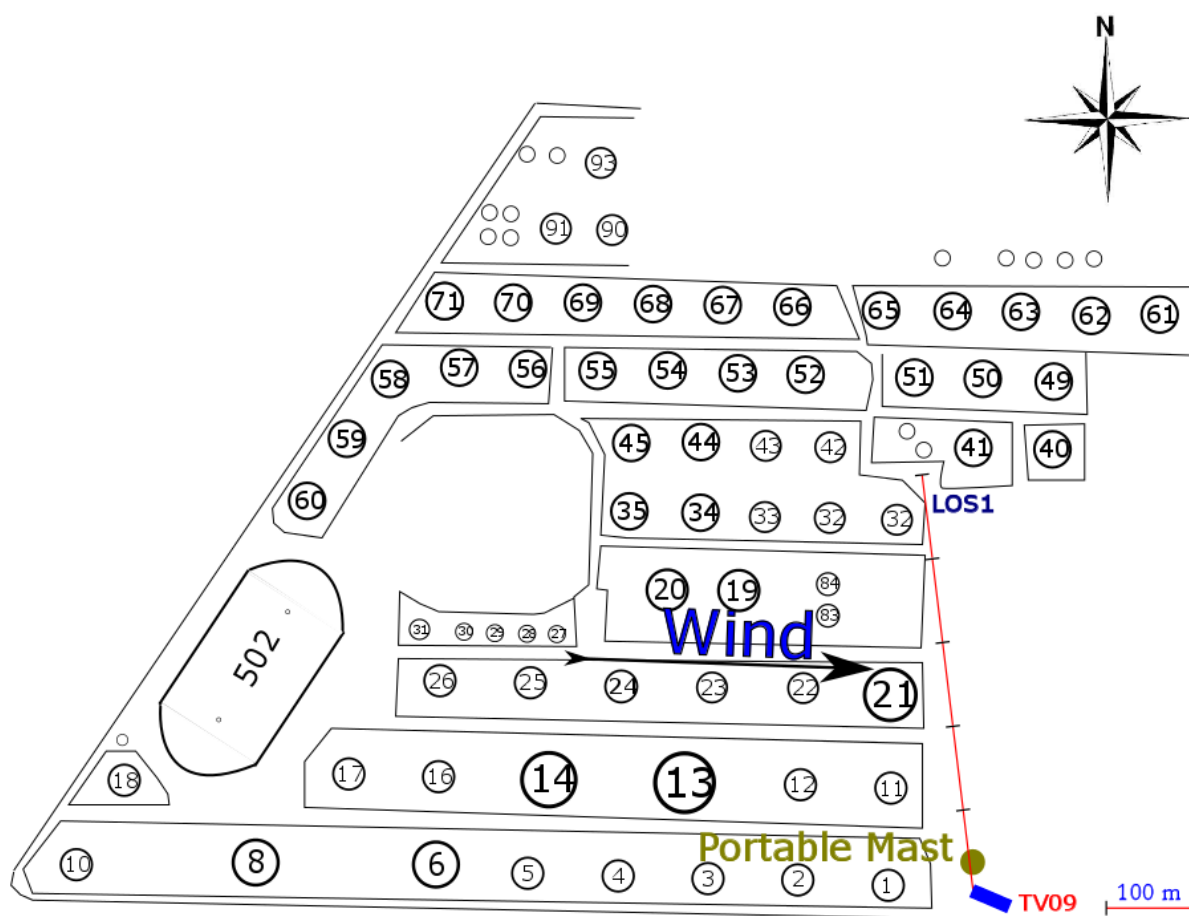
Figure 4.13 Measurement configuration for location TV08 on 6th of October.

Table 4.14 VOC Emission rate determined from TV09 on 6th of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
103	TV09/LOS1	14:48	14:59	4.8	266.3	43.97	Tanks 11,12,13,14,21,22,23,24, 25
104	TV09/LOS1	14:59	15:10	5.7	275.2	73.31	Tanks 11,12,13,14,21,22,23,24, 25
105	TV09/LOS1	15:11	15:21	5.5	272.5	77.78	Tanks 11,12,13,14,21,22,23,24, 25
106	TV09/LOS1	15:22	15:33	5.6	268.6	71.89	Tanks 11,12,13,14,21,22,23,24, 25
107	TV09/LOS1	15:33	15:44	6.0	269.4	55.43	Tanks 11,12,13,14,21,22,23,24, 25
108	TV09/LOS1	15:44	15:54	5.8	277.7	55.59	Tanks 11,12,13,14,21,22,23,24, 25

**Figure 4.14 Measurement configuration for location TV09 on 6th of October.**

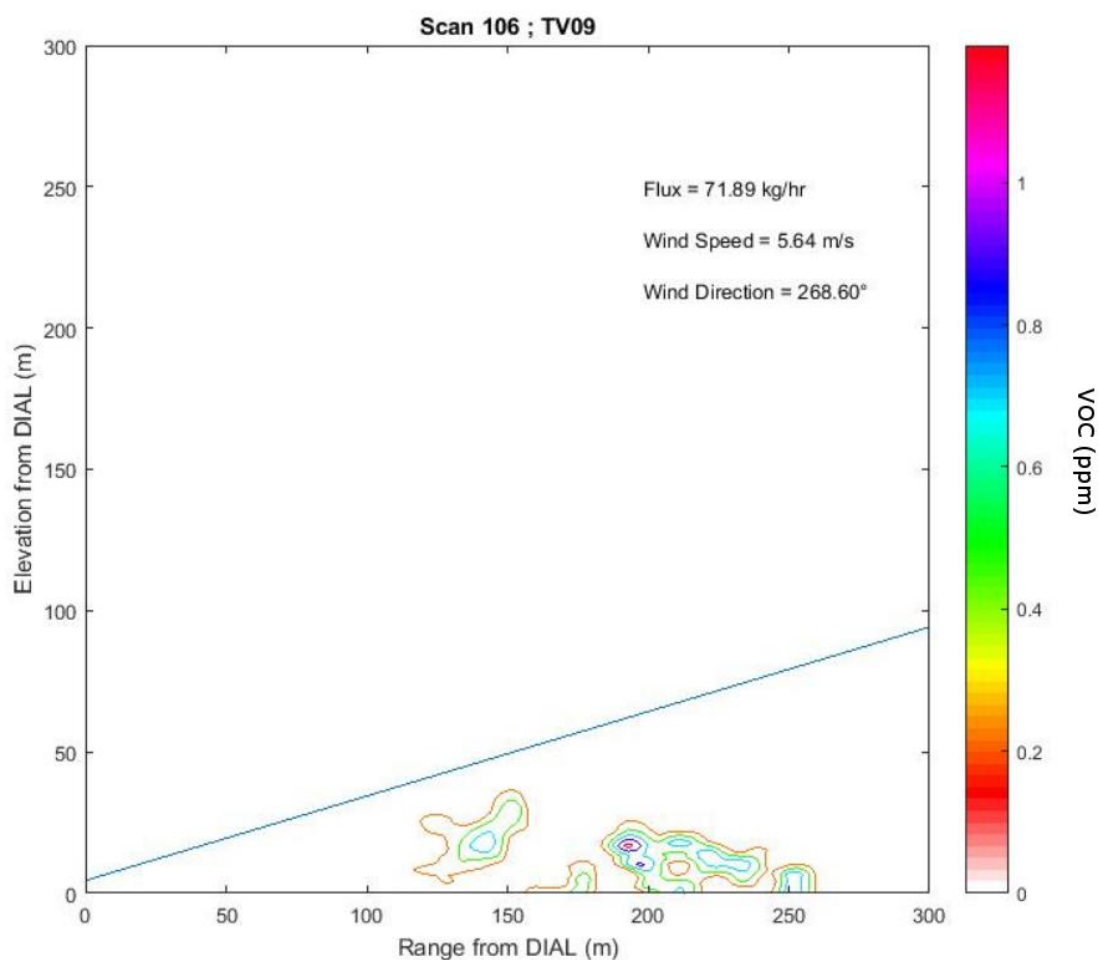


Figure 4.14a1 Observed VOC concentration for Scan 106 representing TV09/LOS1.



Figure 4.14a2 Visualisation of emission rate for Scan 106 representing TV09/LOS1.

Table 4.15 VOC Emission rate determined from TV10 on 7th of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
109	TV10/LOS1	10:10	10:19	1.1	303.3	5.16	Tanks 16,26,31 & North Reservoir 502
110	TV10/LOS1	10:20	10:28	0.8	334.1	3.87	Tanks 16,26,31 & North Reservoir 502
111	TV10/LOS1	10:28	10:37	1.2	294.1	4.38	Tanks 16,26,31 & North Reservoir 502
112	TV10/LOS1	10:42	10:50	0.7	255.9	1.30	Downwind Tanks 16,17,18
113	TV10/LOS2	10:56	11:05	1.6	235.8	2.14	Downwind Tanks 26,17,8
114	TV10/LOS2	11:05	11:15	1.4	280.4	-	Wind Direction Almost Parallel to LOS
115	TV10/LOS2	11:15	11:25	2.2	231.4	2.39	Downwind Tanks 26,17,8
116	TV10/LOS3	11:37	11:45	2.7	255.6	20.96	Tanks 13,14,16,17,18
117	TV10/LOS3	11:46	11:54	2.3	267.7	19.67	Tanks 13,14,16,17,18
118	TV10/LOS3	11:54	12:03	1.8	226.7	9.83	Downwind Tanks 13,3,4,5
119	TV10/LOS3	12:03	12:12	2.0	195.4	12.57	Downwind Tanks 13,3,4
120	TV10/LOS4	12:16	12:24	3.3	183.2	21.97	Downwind Tanks 23,22,13,12,3,2
121	TV10/LOS4	12:24	12:33	3.3	201.4	16.73	Downwind Tanks 23,22,13,12,3,2
122	TV10/LOS4	12:33	12:42	3.2	202.9	22.39	Downwind Tanks 23,22,13,12,3,2
123	TV10/LOS4	12:42	12:51	3.3	181.1	21.66	Downwind Tanks 23,22,13,12,3,2
125	TV10/LOS5	13:04	13:13	2.1	209.9	12.85	Downwind Tanks 29,30,31,26,16,17,6
126	TV10/LOS5	13:14	13:22	2.4	266.7	1.12	Downwind North Reservoir 502

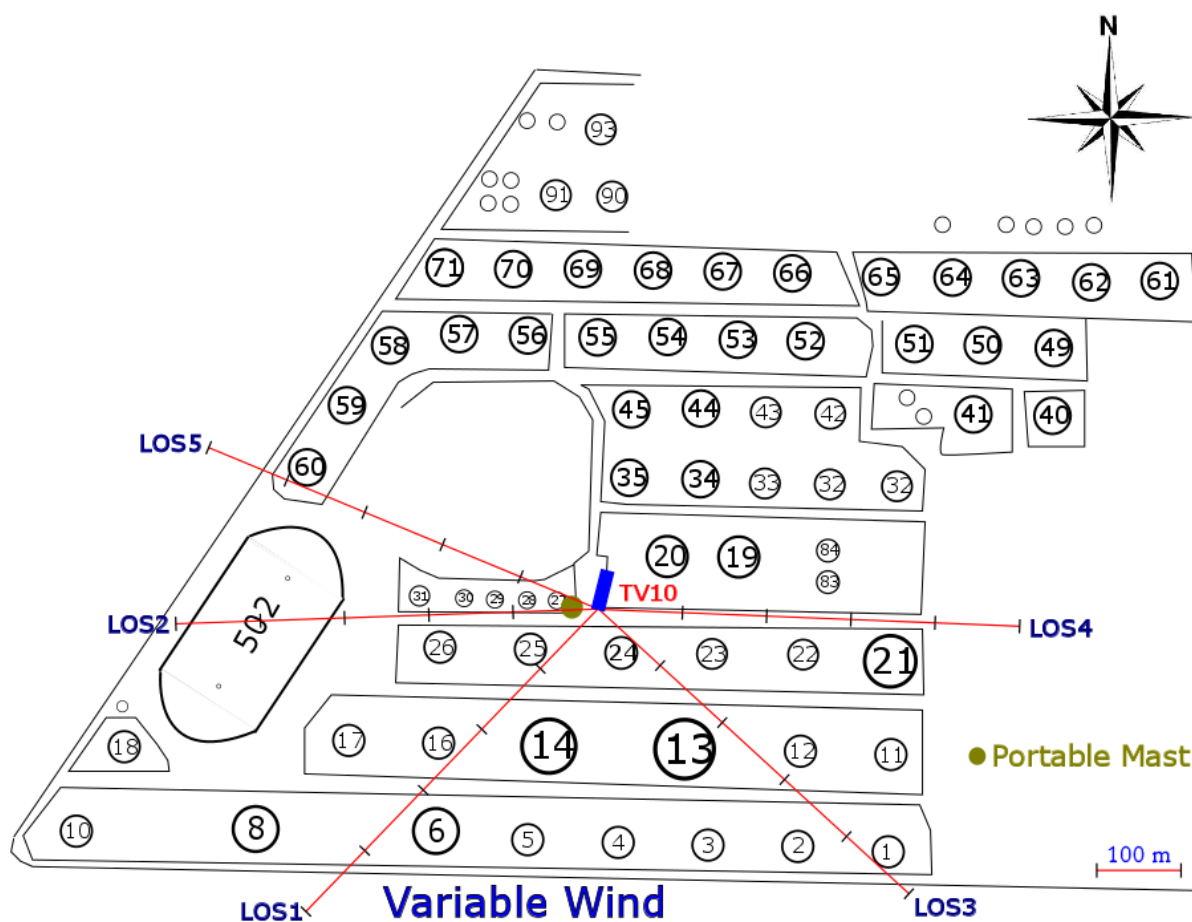
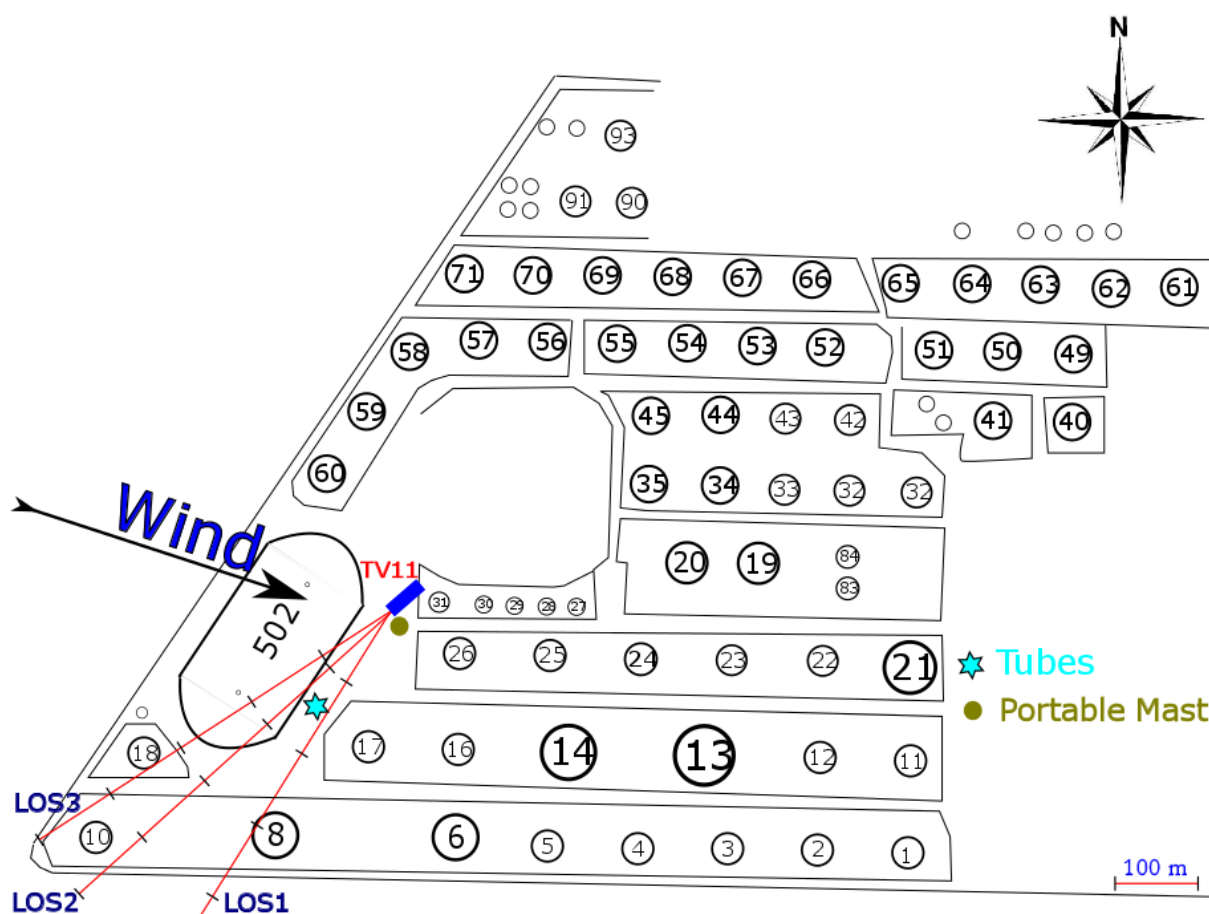
**Figure 4.15 Measurement configuration for location TV10 on 7th of October.**

Table 4.16 VOC Emission rate determined from TV11 on 7th of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed m/s	Wind Direction Degrees	Emission Rate kg/hr	Notes
127	TV11/LOS1	13:53	14:01	3.9	300.7	27.34	Downwind South Area Reservoir 502
128	TV11/LOS2	14:14	14:30	4.4	305.5	41.23	Downwind Reservoir 502 South Vent
129	TV11/LOS2	14:30	14:47	4.2	296.6	29.17	Downwind Reservoir 502 South Vent
130	TV11/LOS2	14:47	15:04	5.2	294.8	50.25	Downwind Reservoir 502 South Vent
131	TV11/LOS2	15:04	15:21	5.7	300.3	54.70	Downwind Reservoir 502 South Vent
132	TV11/LOS3	15:28	15:41	6.1	299.0	54.55	Downwind Reservoir 502 South Vent
133	TV11/LOS3	15:41	15:54	5.8	289.9	66.06	Downwind Reservoir 502 South Vent

Figure 4.16 Measurement configuration for location TV11 on 7th of October.

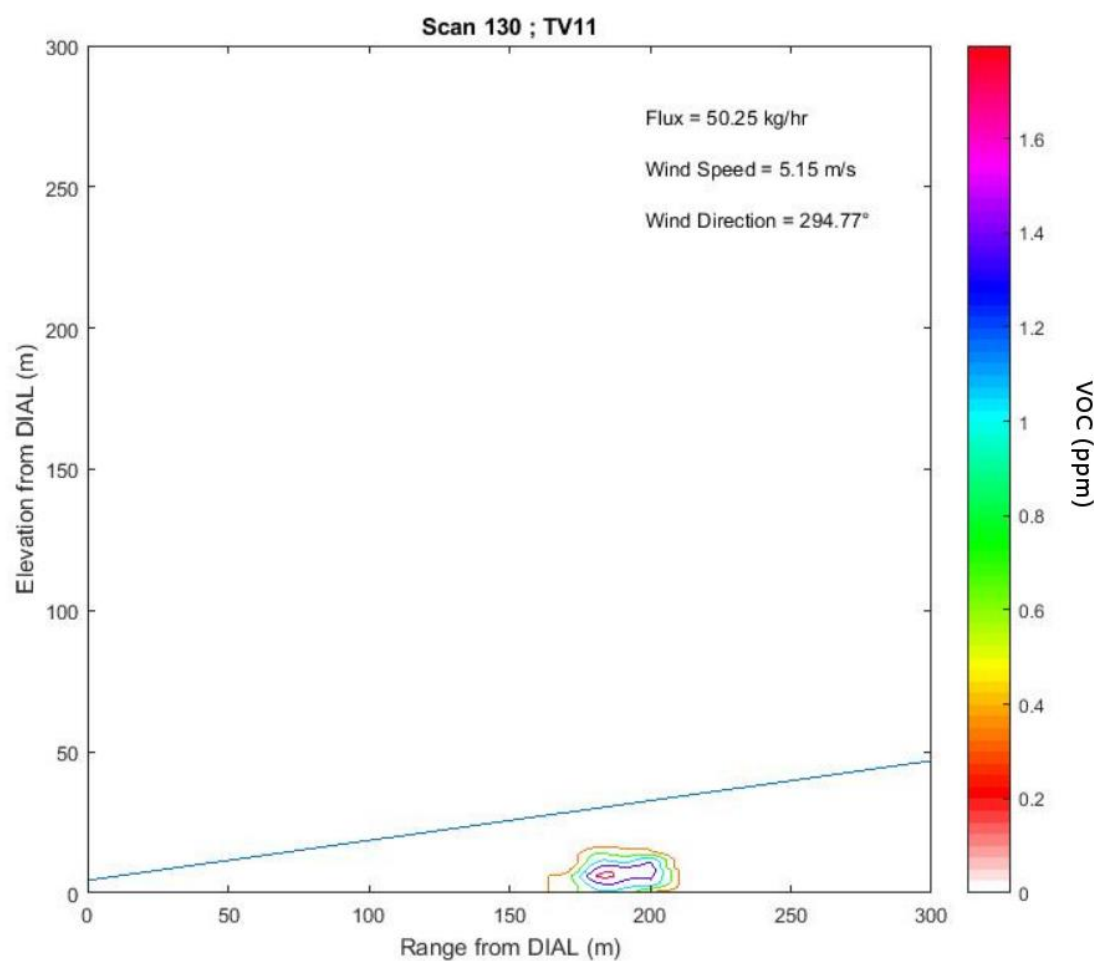


Figure 4.16a1 Observed VOC concentration for Scan 130 representing TV11/LOS2.

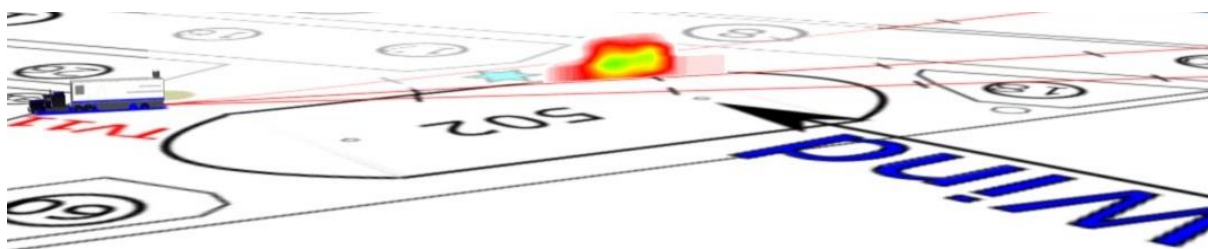


Figure 4.16a2 Visualisation of emission rate for Scan 130 representing TV11/LOS2.

5 RESULTS DISCUSSION FOR BENZENE MEASUREMENTS

Benzene emission measurements from selected parts of the tank farm were performed by DIAL on September 28th and 29th. During this time period, a number of scans downwind of various components of the tank farm were performed. Table 5.1 provides overview of measured Benzene emission fluxes.

Table 5.1 Summary of determined benzene emission rates. For each location and LOS the average flux and standard deviation (when more than one scan is available) are reported.

Date	Location/ LOS	Notes	Average Flux	Standard Deviation	Scans
			kg/hr	kg/hr	#
28-Sep	TB01/LOS1	Downwind Tanks 11,21,22,23,24,19,20,83	0.6	0.3	5
29-Sep	TB02/LOS1	Downwind Tanks 90,91,93	0.1	-	1
29-Sep	TB02/LOS1	Downwind NW Corner Small Tanks & 71	0.0	0.0	2
29-Sep	TB02/LOS1	Downwind Tanks 91,70	0.0	-	1
29-Sep	TB03/LOS1	Downwind Tanks 33,34,35,43,44,45	0.1	-	1
29-Sep	TB03/LOS1	Downwind Tanks 33,34,43,20	0.1	0.0	2
29-Sep	TB03/LOS1	Downwind Tanks 83,84,32,42	0.0	-	1
29-Sep	TB04/LOS1	Downwind Tanks 14,13,12,11,5,4,3,2,1	0.0	0.0	2
29-Sep	TB04/LOS1	Downwind Tanks 6,16	0.0	-	1
29-Sep	TB04/LOS1	Tanks 26,16,17 & Central Area 502	0.2	0.0	4
29-Sep	TB05/LOS1	Tanks 42,52,66,53,67,54,68,69	0.2	0.1	4

The calculations of the benzene emission rate from the different locations are described in the following sections.

5.1 MEASUREMENTS OF THE SOUTH TANK AREA

On the 28th Sept measurements carried out from location TB01/LOS1 with a W/NW wind were downwind of several tanks, as shown in Figure 4.1 and summarized in Table 4.1. The data analysis range was up to 300 m from the DIAL and the average emission rate was 0.6 ± 0.3 kg/hr that includes emissions from Tanks 11, 21, 22, 23, 24, 19, 20, 83 with possible contributions from tanks further upwind. Figures 4.1a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 6. The emission was diffuse with higher concentration values in the 250-300 m region from the DIAL.

On the 29th Sept measurements were made from location TB04/LOS1, see Figure 4.4 and Table 4.4. During the first three scans (18, 19 and 20), the wind was variable from east to southwest and no benzene emission was detected. The wind then shifted to the W/NW allowing to measure the emission rate from Tanks 26, 16, 17 and the central area of Reservoir 502. The average emission rate was 0.2 kg/hr, just above the DIAL benzene detection limit, which, for the conditions during the two measurement days, was about 0.1 kg/hr.

5.2 MEASUREMENTS OF THE NORTH TANK AREA

On the 29th Sept measurements were made from location TB02/LOS1 with light wind speed and variable wind direction, as shown in Figure 4.2 and summarized in Table 4.2. These measurements were downwind the tanks in the NW corner of the tank area and only Scan 7 showed some emission above the DIAL detection limit downwind of Tanks 90, 91 and 93.

Of the measurements made from location TB03/LOS1 with variable wind direction, see Figure 4.3 and Table 4.3, only Scan 13 showed some benzene emission above the DIAL detection limit from Tanks 33, 34, 35, 43, 44 and 45.

The measurements conducted from location TB05/LOS1 with a north-westerly wind were downwind of Tanks 42, 52, 66, 53, 67, 54, 68 and 69, as shown in Figure 4.5 and summarized in Table 4.5. The average benzene emission rate of 0.2 ± 0.1 kg/hr was measured from that part of the tank farm.

5.3 CONCLUSION

During the day and a half of benzene measurements it was possible to observe a number of tanks, but not the entire tank area. The areas of detected emissions above the DIAL detection limit are reported in the summary Table 5.2 and the total benzene emission rate from these areas was determined to be 1.2 ± 0.3 kg/hr. The highest emission rate of 0.6 ± 0.3 kg/hr was measured in the SE tank area, although such emission was relatively low.

Table 5.2 Summary of benzene flux measurements for different site's areas.

Emission Area	Average Flux	Standard Deviation
	kg/hr	kg/hr
Tanks 42,52,66,53,67,54,68,69	0.2	0.1
Tanks 90,91,93	0.1	-
Tanks 33,34,35,43,44,45	0.1	-
Tanks 11,21,22,23,24,19,20,83	0.6	0.3
Tanks 26,16,17 & Central Area 502	0.2	0.0
Total	1.2	0.3

Because tank farm emissions are highly dependent on the tanks content and operation, it is very difficult to draw a parallel between emissions from different refineries tank farms. When benzene is only a small fraction of the product stored in the tank then it will show up only in a small quantity when VOC leaks are detected. In previous DIAL measurements at other refineries tank farms that showed very low and diffuse VOC emissions, normally no benzene emissions were measured above the DIAL detection limit. Conversely, in previous studies benzene emissions were observed above the DIAL detection limit when localised plumes with relatively high VOC emissions (> 10 kg/hr) were detected [Innocenti, 2010].

The reported annual benzene emissions for the entire refinery site in 2015 were 1551.77 pounds per year [SCAQMD FIND, 2016] i.e. an average of 0.08 kg/hr which would be below the best DIAL detection limit of 0.1 kg/hr. This value is about a factor 10 lower than the emission observed by the DIAL during the two measurement days. Such comparison can only be valid if the emission rate measured during a short study was representative of the average annual emissions. Since the emission rates could vary during the year, longer measurements over different periods would be informative to obtain a more accurate comparison between measured and annual reported emissions. It also important to keep in mind that that this factor is based on the measured emissions and does not include any estimate for the unmeasured part of the refinery. Any area that is not measured could only increase or maintain the total emission when measured.

6 RESULTS DISCUSSION FOR VOC MEASUREMENTS

A series DIAL measurements of VOC emissions from various components of the tank farm were performed between October 1 and October 5, 2015. Table 6.1 provides average VOC fluxes from different parts of the tank farm.

Table 6.1 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation (when more than one scan is available) are reported.

Date	Location/ LOS	Notes	Average Flux	Standard Deviation	Scans
			kg/hr	kg/hr	#
1-Oct	TV01/LOS1	Downwind Tanks 29,30,31,26,16,17,6	13.4	3.0	2
1-Oct	TV01/LOS2	Downwind Tanks 58 & 59	7.3	0.9	3
1-Oct	TV02/LOS1	Downwind Reservoir 502 & Tank 17	61.8	6.3	4
2-Oct	TV03/LOS1	Downwind Tanks 3 & 4	1.5	-	1
2-Oct	TV03/LOS1	Downwind Tanks 5 & 14	2.0	-	1
2-Oct	TV03/LOS2	Downwind Tanks 26,16,17,6	3.8	0.8	4
2-Oct	TV03/LOS3	Downwind Tanks 23,22,13,4,3	9.4	1.3	4
2-Oct	TV04/LOS1	Tanks 44,43,34,33,20,19	15.6	-	1
2-Oct	TV04/LOS1	Tanks 45,44,43,35	4.7	-	1
2-Oct	TV04/LOS2	Tanks 68,69,90,91,93 + Small Tanks	28.1	1.6	4
2-Oct	TV05/LOS1	Tanks 53,54,55,56,57,58,43,44,45	20.7	5.1	4
5-Oct	TV06/LOS1	Downwind Tanks 23,22,12,11,1	21.4	4.8	4
5-Oct	TV06/LOS2	Downwind Tanks 14,5,4	3.9	-	1
5-Oct	TV06/LOS3	Downwind Tanks 16,6	280.9	26.7	4
5-Oct	TV06/LOS4	Downwind Tanks 16,6,26,17	271.2	17.9	4
5-Oct	TV06/LOS5	Downwind Tanks 13,12,3,2	20.8	3.4	4
5-Oct	TV07/LOS1	Downwind Tanks 16,6,5	290.3	74.2	4
5-Oct	TV07/LOS1	Downwind Tanks 16,6,5 - No Scan 83	254.2	18.4	3
5-Oct	TV07/LOS2	Downwind Tank 6	2.2	-	1
5-Oct	TV07/LOS3	Downwind Reservoir 502 South Vent	41.2	7.0	3
6-Oct	TV08/LOS1	Downwind Reservoir 502 South Vent	34.7	3.0	2
6-Oct	TV08/LOS2	Downwind Reservoir 502 North Vent	2.7	0.9	7
6-Oct	TV09/LOS1	Tanks 11,12,13,14,21,22,23,24, 25	63.0	13.5	6
7-Oct	TV10/LOS1	Tanks 16,26,31 & North Reservoir 502	4.5	0.7	3
7-Oct	TV10/LOS1	Downwind Tanks 16,17,18	1.3	-	1
7-Oct	TV10/LOS2	Downwind Tanks 26,17,8	2.3	0.2	2
7-Oct	TV10/LOS3	Tanks 13,14,16,17,18	20.3	1.2	2
7-Oct	TV10/LOS3	Downwind Tanks 13,3,4,5	9.8	-	1
7-Oct	TV10/LOS3	Downwind Tanks 13,3,4	12.6	-	1
7-Oct	TV10/LOS4	Downwind Tanks 23,22,13,12,3,2	20.7	2.8	4
7-Oct	TV10/LOS5	Downwind Tanks 29,30,31,26,16,17,6	12.8	-	1
7-Oct	TV10/LOS5	Downwind North Reservoir 502	1.1	-	1
7-Oct	TV11/LOS1	Downwind South Area Reservoir 502	27.3	-	1
7-Oct	TV11/LOS2	Downwind Reservoir 502 South Vent	43.8	11.4	4
7-Oct	TV11/LOS3	Downwind Reservoir 502 South Vent	60.3	8.4	2

The calculations of the VOC emission rate from the different locations are described in details in the following sections.

6.1 MEASUREMENTS OF RESERVOIR 502

Underground Reservoir 502 was an ideal source to perform intercomparison measurements with the other optical remote techniques involved in the project and it was therefore measured on several occasions and on different days.

On October 1st the measurements of Reservoir 502 were carried out from location TV02/LOS1 with a north-westerly wind, as shown in Figure 4.7 and summarized in Table 4.7. The average measured emission rate was 61.8 ± 6.3 kg/hr included emissions from Reservoir 502 and Tank 17. Average emission rate of only 3.8 kg/hr for the group of Tanks 17, 26, 16 and 6, was measured from location TV03/LOS2 on the October 2. Therefore, the contribution from Tank 17 was determined to be negligible, with most of the measured emissions originating from Reservoir 502.

The emission from the south part of Reservoir 502 was measured on the 5th of October from location TV07/LOS3 with a southerly wind. The average emission rate was 41.2 ± 7.0 kg/hr mainly from the south vent of the Reservoir. The south vent was also measured on the 6th from location TV08/LOS1 with a westerly wind (see Figure 4.13 and summarized in Table 4.13). The average emission rate was 34.7 ± 3.0 kg/hr, comparable with the emission measured on 5th. The average emission rate from the north vent on October 5th was 2.7 ± 0.9 kg/hr, as measured from location TV08/LOS2 (see Figure 4.13).

On the 7th Oct the emission from the north area of Reservoir 502 was measured from location TV10/LOS1 (see Figure 4.15) with a NW wind. The average emission rate was 4.5 kg/hr and it included the emission from Tanks 16, 26 and 31. A single measurement of the north area of Reservoir 502 (Scan 126) was made from location TV10/LOS5 with westerly wind and it showed a low emission, 1.1 kg/hr. These emissions are comparable to the ones measured on October 5th, confirming a lower emission from the north vent in comparison with the higher emission from the south vent.

Measurements of the emission from south part of Reservoir 502, and in particular from the south vent, were also repeated on the 7th of October from location TV11 with a W/NW wind (see Figure 4.16 and Table 4.16). Scan 127 along LOS1 was downwind the south part of Reservoir 502 while scans along LOS2 and LOS3 were specifically targeting the emission from the south vent. The emission rate was variable and it appeared to be increasing during the two measurement hours. The average emission rate measured along LOS2 was 43.8 ± 11.4 kg/hr which compares well with the emission measured on October 5th and 6th. The average emission rate measured along LOS3 was 60.3 ± 8.4 kg/hr similar to the emission measured on October 1st for the entire Reservoir 502 area. The overall Reservoir 502 south area average emission rate measured from location TV11 was 46.2 ± 14.3 kg/hr. Figures 4.16a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 130.

To summarise all observations, the south vent was identified as the main emission source for Reservoir 502; during the three sets of measurements its emissions varied from the low of about 27 kg/hr to the high of 66 kg/hr. The average of all the measurements of the south part of Reservoir 502 was 43.0 ± 11.8 kg/hr. The emission from the north area of Reservoir 502 was relatively low, amounting to 2.7 kg/hr. By adding the two areas together, the average emission rate during the measurement campaign from Reservoir 502 was 45.7 ± 11.9 kg/hr. This is consistent with the total emissions of 61.8 ± 6.3 kg/hr measured from Reservoir 502 from location TV02 on the 1st of October. The total emission from Reservoir 502 varied during the measurements period from about 30 kg/hr to 70 kg/hr with the average of all these measurements (including the emission measured from location TV02) is 49.7 ± 12.7 kg/hr with the standard deviation reflecting the DIAL uncertainty and the source variability.

6.2 MEASUREMENTS OF TANK 16

On the 5th of October the DIAL team as well as other remote sensing contractors involved in the project discovered a VOC leak from Tank 16, which provided for an opportunity for intercomparison measurements. Two sets of measurements were made from location TV06 along LOS3 and LOS4 with a southerly wind (see Figure 4.11 and Table 4.11). The average emission rate measured along LOS3 was 280.9 ± 26.7 kg/hr and it includes contributions from Tank 16 and Tank 6. Previous measurements conducted from location TV07/LOS2 (see Figure 4.12) showed that the emission from

Tank 6 were about 2.2 kg/hr (Scan 87, Table 4.12), which was very low compared to the emissions from Tank 16 observed on that day. The average emission rate along LOS4 was 271.2 ± 17.9 kg/hr and it includes the emission from Tanks 26, 16, 17 and 6. The contribution from the other tanks was again determined to be very small since the emission from these tanks measured earlier on the 2nd of October from location TV03/LOS2 (see Figure 4.18) was 3.8 kg/hr. The emission rates from the two sets of TV06 measurements compare well with a standard deviation less than 10% indicating that during this period the leak rate from Tank 16 was approximately stable.

Measurements of Tank 16 were also carried out from location TV07/LOS1 with a southerly wind (see Figure 4.12 and Table 4.12). The average emission rate was 290.3 ± 74.2 kg/hr with a standard deviation higher than the previous two sets of measurements from location TV06, indicating that this time the emission measured from Tank 16 was probably not stable. Particularly, emissions observed from Scan 83 was about 400 kg/hr (see Figure 6.1), which was higher than the emission measured from the other three scans. The average emission rate excluding Scan 83 was 254.2 ± 18.4 kg/hr that compares well with the two average emission rates measured from location TV06; the standard deviation is also smaller and comparable with the standard deviations measured from location TV06. The time series of Tank 16 emission rates is plotted in Figure 6.1 showing a relatively stable emission during DIAL measurements apart from Scan 83 at 14:53. This measurement was carried out an hour and 20 minutes after the last measurement of Tank 16 from location TV06. At any time during this period it is possible the leak emission rate increased and it was captured by the DIAL only during Scan 83 and then the emission rate decreased back to the values previously measured from location TV06. Figures 4.12a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 85.

Due to the site access limitations, DIAL measurements on October 5th were completed for the day at approximately 15:30 local time. Refinery crew, who were informed of the discovery of a leak, repaired this leak later that afternoon. The leak from Tank 16 was not observed for the remainder of the campaign.

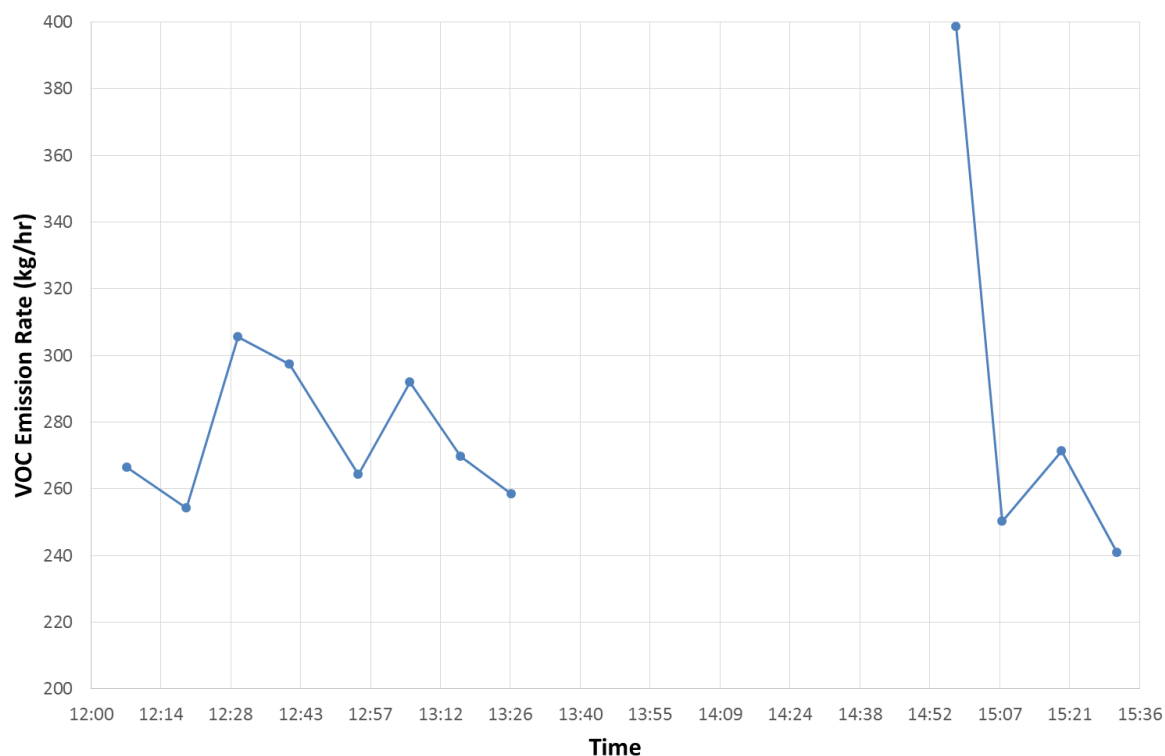


Figure 6.1 VOC emission rate from Tank 16.

6.3 MEASUREMENTS OF OTHER TANKS IN THE NORTH AREA

On October 2nd measurements were carried out from location TV04 with a variable S/SW wind during the two measurements along LOS1 and a more stable northwest wind during measurements along LOS2, see Figure 4.9 and Table 4.9. Scan downwind of Tanks 44, 43, 34, 33, 20, 19 along LOS1 with southerly wind produced the emission rate of 15.6 kg/hr (Scan 55, Table 4.9). Scan downwind of Tanks 45, 44, 43, 35 with a south-westerly wind produced emission flux of 4.7 kg/hr (Scan 56, Table 4.9). By subtracting emission rate measured during Scan 56 from Scan 55 emission rate, it is possible to calculate an estimated emission rate from Tanks 34, 33, 20, 19 which is 10.9 kg/hr. This rate of emissions represents a lower limit of emissions from these tanks because Tank 45 is measured in Scan 56 but not in Scan 55. The average emission flux measured downwind of Tanks 68, 69, 90, 91, 93 and all the small tanks in the NW corner of tank farm area along LOS2 (see Figure 4.9) was 28.1 ± 1.6 kg/hr. Figures 2.9a1 and a2 show a contour plot and a 3D visualisation of the emission as observed from Scan 59 (Table 4.9).

On the 2nd of October measurements downwind of Tanks 53, 54, 55, 56, 57, 58, 43, 44, 45 were also conducted from location TV05/LOS1 with a westerly wind direction, see Figure 4.10 and Table 4.10. The average emission rate was 20.7 ± 5.1 kg/hr.

On the 1st of October measurements downwind of Tanks 58 and 59 were carried out from location TV01/LOS2 with a W/NW wind direction, as shown in Figure 4.6 and summarized in Table 4.6. The average emission flux was 7.3 ± 0.9 kg/hr.

Most of the tanks in the NW area (west of Tank 66) have been measured by the DIAL and the combined average emission rate for this area was determined to be 66.9 ± 5.4 kg/hr.

6.4 MEASUREMENTS OF THE SOUTH PART OF THE TANK PARK AREA

On the 1st of October measurements downwind of Tanks 29, 30, 31, 26, 16, 17, 6 were made from location TV01/LOS1 with a southerly wind, revealing the average emission rate was 13.4 ± 3.0 kg/hr. Figures 4.6a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 30 (see Table 4.6). Measurements of the same tank area from location TV10/LOS5 and a southerly wind produced similar emission flux of 12.8 kg/hr (Scan 125, Table 4.15). The overall average emission rate from Tanks 29, 30, 31, 26, 16, 17, 6 was 13.2 ± 1.1 kg/hr. Most of this emission can be associated with Tanks 29, 30, 31 as the emission from Tanks 26, 16, 17, 6 was measured separately from location TV03/LOS2 and the average emission rate was relatively small, 3.8 ± 0.8 kg/hr.

On the 6th of October measurements downwind of Tanks 11, 12, 13, 14, 21, 22, 23, 24 and 25 were made from location TV09/LOS1 with a westerly wind, as shown in Figure 2.14 and summarized in Table 2.14. The average emission rate was 63.0 ± 13.5 kg/hr and Figures 2.14a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 106 (see Table 4.14).

The measurements outlined above together with Reservoir 502 measurements described in Section 6.1 envelope most of the south tank area apart from the southern-most row of tanks (Tanks 3, 4, 5, 10, and 14). Several of these tanks were measured together with other tanks showing a relatively low emission rate. For example, flux measured downwind of Tanks 3 and 4 from location TV03/LOS1 during south-easterly wind was 1.5 kg/hr (Scan 43, Table 4.8). Similarly, scan downwind of Tanks 14 and 5 along the same LOS1, but with a south-westerly wind measured a low emission flux, 2.0 kg/hr (Scan 45, Table 4.8). A low emission of 3.9 kg/hr from Tanks 14, 5, 4 was also measured from location TV06/LOS2. Tank 18 was measured together with Tanks 16 and 7 from location TV10/LOS1 (Scan 112) and a south-westerly wind with an emission rate of 1.3 kg/hr. A small emission, 2.3 ± 0.2 kg/hr, was also measured from Tank 8 including the emission from Tanks 26 and 17 (Scan 115). Overall, of the south tank area only Tank 10 was not included in any of the DIAL measurements.

The remaining measurements of the south tank area were consistent with each other, mainly showing significant emission when Tanks 12 and 13 were included in the measurements. On the 2nd of October Tanks 23, 22, 13, 4, 3 were measured from location TV03/LOS3 and S/SW wind, see Figure 4.8 and summary Table 4.8; the average emission rate was 9.4 ± 1.3 kg/hr. On the 5th of October measurements were made from location TV06/LOS1 downwind of Tanks 23, 22, 12, 11, and 1 with a south-easterly wind (see Figure 2.11 and Table 2.11), the average emission rate was 21.4 ± 4.8 kg/hr. The measurements carried out from location TV06/LOS5 with a southerly wind were downwind of Tanks 13, 12, 3, 2 with an average emission rate of 20.8 ± 3.4 kg/hr.

On the October 7th measurements were carried out from location TV10 with a variable wind direction as shown in Figure 2.15 and summarized in Table 2.15. Measurements along LOS3 with a westerly wind were downwind of Tanks 13, 14, 16, 17, 18 and the average emission rate was 20.3 ± 1.2 kg/hr. Scan 118 along LOS3 with a southwest wind was downwind of Tanks 13, 3, 4, 5 while Scan 119 with a more southerly wind was downwind of Tanks 13, 3, 4. The measured emissions were similar, 9.8 kg/hr and 12.6 kg/hr respectively. Scans along LOS4 and southerly wind direction were downwind of Tanks 23, 22, 13, 12, 3, 2; the average emission rate was 20.7 ± 2.8 kg/hr.

Overall VOC emission from the south tank area can be estimated at 127.5 ± 18.6 kg/hr obtained by adding the emissions from Reservoir 502, Tanks 29,30,31,26,16,17,6, Tanks 11,12,13,14,21,22,23,24, 25 and Tanks 3, 4. Although this does not include a specific contribution from Tanks 8, 5, 4 and 1, it was concluded from the measurements described above that these tanks were not significant emission sources.

6.5 CONCLUSION

DIAL VOC measurements of the tank farm area were carried out over four and a half days. Approximately half of the time was spent on repeated measurements of the same sources for the purpose of direct intercomparison measurements with other ORS techniques involved in the project. The sources used for the validation/intercomparison exercise were Reservoir 502, which was measured on several occasions on different days, and Tank 16 that had a high emission leak for most of the 5th October. The rest of the time was used to determine emission rates from as much of the tank farm area as possible. Most of the tank area was measured, with the exception of a few NE tanks, and the best estimate of the total emission is 194.4 ± 19.4 kg/hr as reported in Table 4.2.

Table 4.2 Summary of VOC flux measurements for different areas of the tank farm.

Emission Area	Average Flux	Standard Deviation
	kg/hr	kg/hr
Tanks 68,69,90,91,93 + NW Small Tanks	28.1	1.6
Tanks 34,33,20,19	10.9	-
Tanks 53,54,55,56,57,58,43,44,45	20.7	5.1
Tanks 58 & 59	7.3	0.9
Reservoir 502	49.7	12.7
Tanks 29,30,31,26,16,17,6	13.2	2.1
Tanks 11,12,13,14,21,22,23,24, 25	63.0	13.5
Tanks 3, 4	1.5	-
Total	194.4	19.4

Similar to the benzene measurements, the highest VOC emission rate was measured in the SE tank farm area. The south vent of Reservoir 502 was the single highest continuous emission source of VOCs, and it had a variable emission rate during the measurement periods. The total emission from Reservoir 502 varied from the low of about 30 kg/hr to the high of 70 kg/hr and Table 4.2 reports the average of all the DIAL measurements.

The values above summarise the long-term emissions from the site and exclude the short-term high levels of emission from the leak in Tank 16 observed on October 5th. The average VOC emission rate during the measurements of the leaking Tank 16 was 280.8 ± 41.9 kg/hr. This includes the emission measured from Scan 83 which was about 40% higher than the emission measured from the other 11 scans that showed a stable emission rate. Scan 83 was made an hour and 20 minutes after the previous measurement of Tank 16. It is possible that during this time the leak emission rate further increased and only the tail-end of this increase was captured by the DIAL during Scan 83 before the emission level decreased back to the previous measurements value. The average emission rate calculated excluding the emission from Scan 83 was 270.1 ± 20.4 kg/hr.

The reported annual VOC emissions for the entire refinery site in 2015 were 440.4 tons per year [SCAQMD FIND, 2016] i.e. averaging 45.6 kg/hr. This value is about a factor 4 lower than the emission observed by the DIAL during the five measurement days. Such comparison can only be valid if the emission rate measured during a short study was representative of the average annual emissions. Since the emission rates could vary during the year, longer measurements over different periods would be informative to obtain a more accurate comparison between measured and annual reported emissions. It should be noted that this factor is based on the measured emissions which do not include any estimate for the unmeasured part of the site and with the short-term leak from Tank 16 excluded. Any area that is not measured could only increase or maintain the total emission when measured.

7 CONCLUSIONS

The goal of this project was to characterise and quantify VOC and benzene emissions from the refinery tank farm area using DIAL method, as well as to use the DIAL facility for intercomparison/validation with other ORS techniques participating in the project.

The measurements showed that the DIAL can easily separate emissions from different areas and individual components of the tank farm and can also identify the main emission sources during various meteorological conditions. During the project, the DIAL demonstrated its capability of to quickly move location in order to adjust to changing atmospheric conditions and to quantify emissions from the tanks, which is a particular advantage especially during periods with light and variable wind, when other ORS methods did not perform well.

Although during the seven measurements days a significant amount of time was spent on repeat measurements of the same sources in order to carry out direct intercomparison measurements with other ORS techniques, the DIAL was still able to measure most of the tank farm in both VOC and benzene configuration. The best estimate of the total emission of the measured area is 194.4 ± 19.4 kg/hr and 1.2 ± 0.3 kg/hr for VOC and benzene respectively.

The highest VOC and benzene emission rates were measured in the south east part of the tank area with the single highest continuous VOC emission source being the south vent of Reservoir 502 which had a variable emission rate during the measurement periods from about 30 kg/hr to 70 kg/hr. Tanks 12 and 13 on the south-east part of the tank farm were also identified as significant VOC sources.

On October 5th a VOC leak event was detected from the Tank 16. This event was measured by DIAL from two different locations and a total of twelve scans spanning over two hour-and-a-half periods were made. Eleven of these scans showed a stable emission rate while one scan that was made an hour and 20 minutes after the previous measurement showed a higher emission rate. The reason for this increase is unclear. The average VOC emission rate calculated excluding this scan was 270.1 ± 20.4 kg/hr. while the average VOC emission rate from all the scans of Tank 16 was 280.8 ± 41.9 kg/hr. Refinery staff was alerted of the leak, which lead to the leak being repaired a few hours later. This event therefore serves as a great example of usefulness of DIAL method for rapid detection of a leak, which otherwise could have gone unnoticed for prolonged period of time.

Reservoir 502 and leaking Tank 16 were sources selected for validation and intercomparison with other remote sensing techniques participating in the project. The results of these activities are presented in separate report by Pikelnaya et al. [in preparation].

The reported hourly averaged refinery 2015 VOC and benzene emissions (calculated from the reported annual emissions) were equivalent to 45.6 kg/hr and 0.08 kg/hr respectively [SCAQMD FIND, 2016]. This values are about a factor 4 for VOC and 10 for benzene lower than the emission observed by the DIAL during the six measurement days. Such comparison can only be valid if the emission rate measured during a short study was representative of the average annual emissions. Since the emission rates could vary during the year, longer measurements over different periods would be informative to obtain a more accurate comparison between measured and annual reported emissions. It should be noted that these factors are solely based on the measured emissions and do not include any estimate for the unmeasured part of the refinery, and with the short-term leak from Tank 16 excluded. Any area that is not measured could only increase or maintain the total emission when measured, as a consequence, the total VOC and benzene emissions from the facility can be potentially higher.

Among all sources surveyed during the campaign, only a small number of localised sources, such as Reservoir 502 and the SE tanks, particularly Tanks 12 and 13, account for the majority of the measured emissions. Efforts to minimise emissions from these sources and to improve the emission factors would allow the estimated and measured emissions to converge. This can be achieved by regular surveys of the site, for example by a comprehensive ORS measurements conducted every few

years. A regular full screening and quantification of site emissions should be undertaken with an appropriate combination of complementary ORS methods to identify leaks that would otherwise not be captured with conventional methods. The results of such ORS surveys also can be used for trend evaluation in time, as well as for cross checking and updating/validation of the ongoing leak-detection and maintenance programs.

The work presented in this report provides SCAQMD with enhanced emission data with low detection limits and high temporal resolution. This data will help to improve emission inventory estimates by narrowing the gap between measured and reported fugitive emission levels from refineries. The results of this study can also provide valuable input for developing future attainments/control strategies and environmental decision-making. In addition, measured data on VOC emissions can be used by SCAQMD to refine its air quality forecasting capabilities by better predicting ozone and particle formation in the South Coast Basin.

8 REFERENCES

Innocenti F; Robinson R; Gardiner T; J Wang, Differential Absorption Lidar (DIAL) Measurements of VOC and Benzene Emissions from a Refinery Site in Houston, TX, US, January/February/March 2010, https://www3.epa.gov/ttnamti1/files/20072008csatam/Houston_dial_appendixa.pdf

Pikelnaya O., Polidori A., Mellqvist J., Samuelsson J., Brohede S., Robinson R., Innocenti F., Helmore J., Hashmonay R., Perry S., Scotto R., Minnich T., (in preparation), Evaluation of Optical Remote Sensing Methods for Volatile Organic Compounds by a Controlled-Release Experiment and Side by Side Measurements, contact O Pikelnaya at opikelnaya@aqmd.gov or A. Polidori at apolidori@aqmd.gov for the copy of the report.

Robinson R; Gardiner T; Innocenti F; Woods P; and Coleman M, Infrared Differential Absorption Lidar (DIAL) Measurements of Hydrocarbon Emissions. J. Environ. Monit., 2011, DOI: 10.1039/C0EM00312C.

South Coast Air Quality Management District (SCAQMD), Facility Information Detail (FIND) system, http://www3.aqmd.gov/webappl/fim/prog/emission.aspx?fac_id=174655, accessed 05-18-16.

9 APPENDIX 1: DESCRIPTION OF THE DIAL TECHNIQUE

9.1 OVERVIEW OF THE DIAL TECHNIQUE

The Differential Absorption Lidar (DIAL) technique is a laser-based remote monitoring technique which enables range-resolved concentration measurements to be made of a wide range of atmospheric species. This section explains the theory of the DIAL technique and describes the NPL system in detail.

9.2 DESCRIPTION OF THE THEORY OF DIAL MEASUREMENTS

The atmospheric return signal, P , measured by a DIAL system from range r and at wavelength x is given by the Light Detection and Ranging (Lidar) equation, a simplified form of which is given in Equation 1.

$$P_x(r) = E_x \frac{D_x}{r^2} B_x(r) \exp\{-2 \int_0^r [A_x(r') + \alpha_x C(r')] dr'\} \quad (1)$$

where D_x is a range independent constant, $C(r)$ is the concentration of an absorber with absorption coefficient α_x and $A_x(r)$ is the absorption coefficient due to all other atmospheric absorption, E_x is the transmitted energy and B_x is the backscatter coefficient for the atmosphere.

The equation has three basic components:

- a backscatter term based on the strength of the signal scattering medium
- parameters associated with the DIAL system
- a term which is a measure of the amount of absorption of the signal which has occurred due to the presence of the target species.

In the DIAL technique, the laser is operated alternately at two adjacent wavelengths. One of these, the "on-resonant wavelength", is chosen to be at a wavelength which is absorbed by the target species. The other, the "off-resonant wavelength", is chosen to be at a wavelength which is not absorbed significantly by the target species, and is not interfered with by other atmospheric constituents.

Pairs of on- and off-resonant signals are then acquired and averaged separately until the required signal to noise ratio is achieved.

The two wavelengths used are close together, hence the atmospheric terms $A_x(r)$ and $B_x(r)$ in the lidar equation can be assumed to be the same for both wavelengths. These terms are then cancelled by taking the ratio of the two returned signals.

The path-integrated concentration (CL) may be derived (Equation 2) by multiplying the logarithm of the ratio of the signals by the ratio of the absorption of the two wavelengths by the target species.

$$CL(r) = \frac{1}{2\Delta\alpha} \frac{1}{N} \sum_{i=1}^N \log \frac{S_{ON,i}(r)}{S_{OFF,i}(r)} \quad (2)$$

where N is the number of pulse pairs averaged, $\Delta\alpha = \alpha_{OFF} - \alpha_{ON}$ is the differential absorption coefficient and S represents the received power after energy normalisation of the on- and off-resonant signals respectively.

This path-integrated concentration represents the total concentration of the target species in the atmosphere along the measured line-of-sight out to the range r .

The range-resolved concentration can then be derived by differentiating the path-integrated concentration (Equation 3).

$$C(r) = \frac{dCL(r)}{dr} \quad (3)$$

where $C(r)$ is the concentration at range r along the line-of-sight averaged over the spatial resolution of the DIAL along its line-of-sight (typically 3.75 m).

9.3 DESCRIPTION OF FACILITY OPERATED BY NPL

The DIAL system operated by NPL is housed in a mobile laboratory. It can operate in the infrared and ultraviolet spectral regions allowing coverage of a large number of atmospheric species. A scanner system directs the output beam and detection optics, giving almost full coverage in both the horizontal and vertical planes.

The system also contains ancillary equipment for meteorological measurements, including an integral 12 m meteorological mast with wind speed, direction, temperature and humidity measurements.

The system is fully self-contained, with power provided by an on board generator, and has full air conditioning to allow operation in a range of ambient conditions.

The following sections describe the DIAL system in more detail.

Source

The source employs a combination of Nd-YAG and dye lasers together with various non-linear optical stages to generate the tuneable infrared and ultraviolet wavelengths. The source has a pulse repetition rate of 10 Hz and an output laser pulse duration of ~10 ns. A small fraction of the output beam in each channel is split off by a beam splitter and measured by a pyroelectric detector (PED) to provide a value for the transmitted energy with which to normalise the measured backscatter return.

Detection

The returned atmospheric backscatter signal is collected by the scanning telescope. This directs the collected light into separate paths for the infrared and ultraviolet channels. The returned light passes through band pass filters relevant to each detection channel and is then focused onto the detection elements. Solid-state cryogenically-cooled detectors are used in the infrared channel and low-noise photomultipliers in the ultraviolet.

After amplification the signals from these detectors are digitised using a high speed digitiser. The digitiser is clocked using a clock generator triggered by the same trigger used to fire the lasers. This ensures the range gating is correctly synchronised to the laser pulse transmission. The signals from the PED monitoring the transmitted energy are also digitised and stored.

Data Analysis

The data acquired are analysed, using the DIAL techniques described below, to give the range-resolved concentration along each line-of-sight.

The data analysis process consists of the following steps:

i) Background subtraction

Any DC background value is subtracted from the signals. This measured background takes account of any DC signal offset which may be present due to electronic offsets and from incident background radiation. The background level is derived from the average value of the far field of the returned lidar signal where no significant levels of backscattered light is present.

ii) Normalisation for variation in transmitted energy

The two signal returns are normalised using the monitored values of the transmitted energy for the on and off resonant wavelength pulses. The mean transmitted energy is used to normalise the averaged return signal. For this application, this has been shown to be equivalent to normalising individual shots against transmitted energy and then averaging the normalised values.

iii) Calculation of path-integrated concentration

The path-integrated concentration of the target species, out to the range r , is calculated using equation 2.

The absorption coefficients used in this calculation are derived from high-resolution spectroscopy carried out using reference gas mixtures at NPL.

iv) Derivation of range-resolved concentrations.

The integrated concentration profiles are piecewise differentiated with a selectable range resolution, to give the range-resolved concentration along the line-of-sight, as in equation 3.

v) Calculation of emission rates

Range-resolved concentration measurements along different lines-of-sight are combined to generate a concentration profile. This is carried out using algorithms developed at NPL which reduce artefacts due to the difference in data density at different ranges, due to the polar scanning format of the data. The emission rate is then determined using the concentration profile together with meteorological data.

The emitted rate is calculated using the following mathematical steps:

- (a) The product is formed of the gas concentration measured with the DIAL technique at a given point in space, and the component of the wind velocity perpendicular to the DIAL measurement plane at the same location, taking into account the wind speed profile as a function of elevation.
- (b) This product is computed at all points within the measured concentration profile, to form a two-dimensional array of data.
- (c) This array of results is then integrated over the complete concentration profile to produce a value for the total emitted rate.

Considerable care is needed in applying the meteorological data, particularly when the concentration profile measured by the DIAL technique has large spatial variations since, for example, errors in the wind speed in regions where large concentrations are present can affect the accuracy of the results. A logarithmic wind profile is used to describe the vertical distribution of the wind. Wind speeds at different heights, usually from the fix mast sensors, are used to calculate the wind profile. The calculated wind field is then combined with the measured gas concentration profile using the procedure described above.

A summary of the ultraviolet and infrared performance capabilities of the NPL DIAL facility are given in Tables A1.1 and A1.2. The values given in these tables are based on the actual levels of performance of the system obtained during field measurements, rather than calculations based on theoretical noise performances. For simplicity the numbers are presented as a single concentration sensitivity and maximum range values. However, the detailed performance behaviour of a DIAL system is much more complex and there are a number of key points that should be noted:

- The DIAL measurement is of concentration per unit length rather than just concentration. So the sensitivity applies for a specified pathlength – 50 metres in this case. Measurements over a

shorter path would have a lower sensitivity, and would be more sensitive over a longer path length.

- Since the backscattered lidar signal varies with range, generally following a $(\text{range})^{-2}$ function, the sensitivity is also a function of range. The sensitivity values given in the tables apply at a range of 200 metres, and these will get poorer at longer ranges.
- The maximum range of the system is generally determined by the energy of the emitted pulse and the sensitivity of the detection system, except in the case of nitric oxide where range is limited by oxygen absorption at the short ultraviolet wavelengths required for this species.
- In all cases the performance parameters are based on those obtained under typical meteorological conditions. For the ultraviolet measurements the meteorological conditions do not have a great effect on the measurements as the backscattered signal level is predominantly determined by molecular (Rayleigh) scattering, and this does not vary greatly. However, in the infrared the dominant scattering mechanism is from particulates (Mie scattering). So the signal level, and therefore the sensitivity, is dependent on the particular loading of the atmosphere, and this can vary dramatically over relatively short timescales.
- The optical configuration of the DIAL system means there is a minimum range between 40-100 m before measurements can be made.

The NPL DIAL has a theoretical range resolution of 3.75 metres along the measurement beam, and a vertical and horizontal scan resolution which can be less than 1 metre at 100 metres. However, the actual range resolution determined by the signal averaging used, will depend on atmospheric conditions and the concentration of the measured pollutant, and may be of the order of 20-30 m.

Table A1.1 Ultraviolet capability of NPL DIAL Facility

Species	Sensitivity⁽¹⁾	Maximum range⁽²⁾
Nitric oxide	25 ppb	500 m
Sulphur dioxide	10 ppb	3 km
Ozone	5 ppb	2 km
Benzene	10 ppb	800 m
Toluene	10 ppb	800 m

Table A1.2 Infrared capability of NPL DIAL Facility

Species	Sensitivity⁽¹⁾	Maximum range⁽²⁾
Methane	50 ppb	1 km
Ethane	20 ppb	800 m
Ethene	10 ppb	800 m
Ethyne	40 ppb	800 m
General hydrocarbons	40 ppb	800 m
Hydrogen chloride	20 ppb	1 km
Methanol	200 ppb	500 m
Nitrous oxide	100 ppb	800 m

(1) The concentration sensitivities apply for measurements of a 50 metre wide plume at a range of 200 metres, under typical meteorological conditions.

(2) The range value represents the typical working maximum range for the NPL DIAL system.

9.4 GENERAL HYDROCARBON SCALING FACTOR

The DIAL is able to make measurements of a wide range of compounds, including benzene and other aromatics, individual VOCs and total VOCs, see Tables A1.1 and A1.2. The methodology for obtaining measurements of the total VOC content from C3 to C15 is provided below. It consists of the combination of DIAL measurements with air sampling and GC analysis. The system is able to monitor individual aromatic compounds and VOC species, which have absorption features in the IR and UV spectral regions covered by the DIAL system. NPL has the spectral expertise, access to spectral libraries and an in-house spectroscopic capability to assess the DIAL sensitivity for additional individual species.

The general hydrocarbon measurement listed in Table A1.2 uses an infrared absorption that is similar for all hydrocarbons with three or more carbon atoms, linked to the stretch frequency of the carbon-hydrogen bond. The line strengths for these species are proportional to the number of carbon-hydrogen bonds present and this enables a total mass emission to be determined. As such it provides a measure of the mixture of volatile organic compounds (VOCs) that are present at an oil or petrochemical site. The pair of infrared wavelengths used for this DIAL measurement are selected so that the absorption per unit mass is relatively invariant with respect to the mix of different hydrocarbons that are present. However, the sensitivity of this measurement in terms of ppb of hydrocarbon depends on the mixture of species present, and the value given in the table reflects the typical mix of hydrocarbons found at oil refineries.

Although the general hydrocarbon measurement provides a good estimate of the overall amount of hydrocarbons present, the accuracy of this measurement can be improved, and the total VOC concentration calculated, by combining the DIAL measurements with the results of gas chromatography (GC) analysis of the emitted gases. The standard procedure for this involves taking whole air samples around the site in locations where the DIAL measurements show the emitted plumes are present. The VOCs present in these samples are identified and quantified by GC analysis. The results provide the relative levels of all the VOCs present with a concentration of 0.1 ppb or higher. The results of this analysis are combined with NPL's unique spectral library of quantified infrared absorptions of an extensive set of VOCs to calculate the combined absorption coefficient for the actual VOC mixture present at the site. Applying this absorption coefficient to the DIAL results enables the total VOC emission rates to be calculated.

9.5 RELATIONSHIP BETWEEN EMISSION RATE AND CONCENTRATIONS

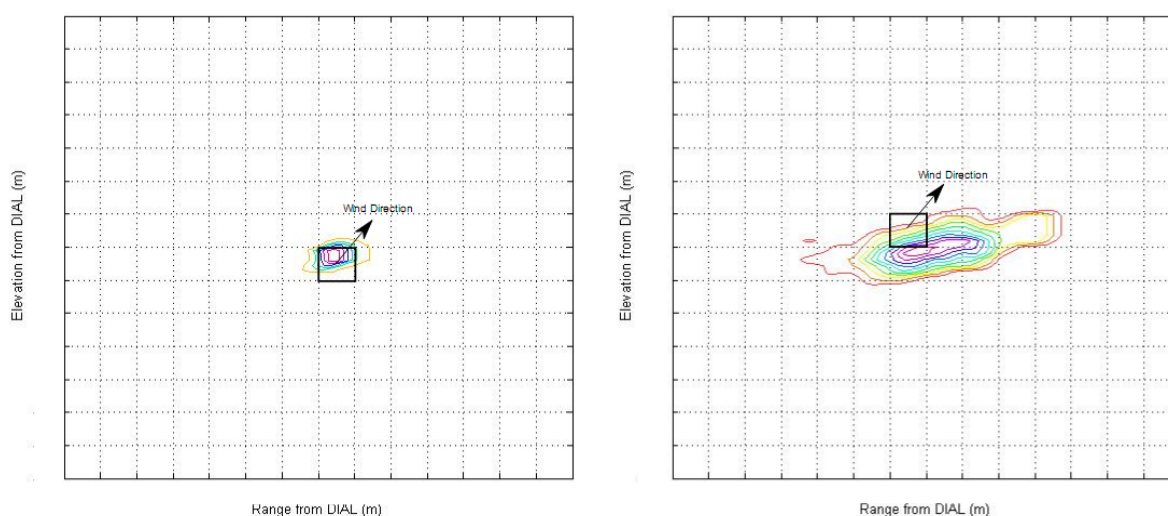


Figure A1.1 Illustration of the emission rate calculation approach

Where concentrations are provided as an indication of the levels observed in a measurement scan, the reported concentration in the measurement plane is the maximum concentration seen in a cell in the measurement plane. The resolution of the planes used is equal to the DIAL system resolution and is 3.75 m, so each cell is 3.75 m square. Figure A1.1 shows how plume size affects the emission rate that is calculated. The concentration assigned to each cell is multiplied by the perpendicular wind field determined for that cell, and then the individual cell emission rates are summed to give the total emission rate through the plane. This figure shows two example plumes (the cell grids are for indication and are not to scale), one which has a small plume, and therefore a small integrated emission rate, and the other which has a larger plume, and therefore represents a larger emissions rate, although the peak concentration in both is similar, and indeed may even be higher in the small plume than the large plume.

Figure A1.2 shows a schematic representation of two measurement plane configurations observing the same plume. One has a nearly perpendicular orientation to the plume, and the wind direction is therefore also perpendicular to the measurement plane. The other is at an angle through the plume, and therefore the wind is not perpendicular to the plane of the measurements. If only the concentration profile were observed the right hand measurement configuration would show a larger plume (as it cuts obliquely through the plume). However, when the wind direction is taken into account, the normal component of the wind vector is used, and this therefore reduces the emission rate determined from this scan, resulting in the same emission rate being determined for both measurement orientations.

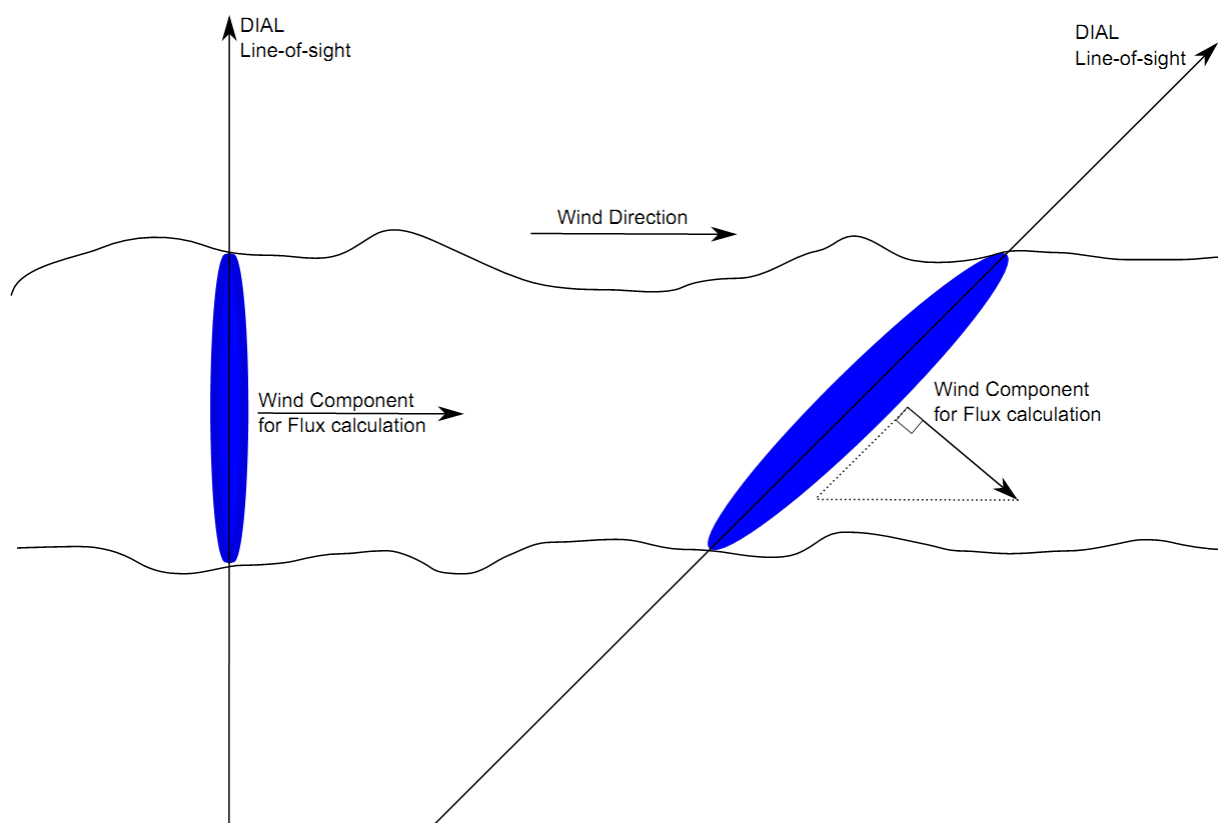


Figure A1.2 Schematic showing relationship between emission rate and wind direction

9.6 CALIBRATION AND VALIDATION

The NPL DIAL system has several in-built calibration techniques and procedures. The most important are the in-line gas calibration cells. The gas cells are filled with known concentrations of the target species, obtained from NPL standard gas mixtures, which are directly traceable to national standards. A fraction of the transmitted beam is split off and directed through a gas cell to a PED, in the same

way as with the beam for the transmitted energy monitors. This provides a direct measurement of the differential absorption at the operating wavelengths by the target gas. The transmission through the gas cells is continuously monitored during the operation of the system to detect any possible drift in the laser wavelengths. The calibration cells are also periodically placed in the output beam to show the concentration response of the whole system is as expected.

A number of field comparisons have been undertaken to demonstrate the accuracy of the measurements obtained with DIAL. Examples of these carried out by NPL are summarized below:

- i) Intercomparisons have been carried out on chemical and petrochemical plants where a large number of different volatile organic species are present. In these intercomparisons, the DIAL beam was directed along the same line-of-sight as a line of point samplers. The point samplers were operated either by drawing air into internally-passivated, evacuated gas cylinders or by pumping air at a known rate, for a specified time, through a series of absorption tubes which efficiently absorb all hydrocarbon species in the range $C_2 - C_8$. The results obtained for the total concentrations of VOCs measured by the point samplers and those measured by the infrared DIAL technique agreed within $\pm 15\%$. The concentrations of atmospheric toluene measured by the ultraviolet DIAL system agreed with those obtained by the point samplers to within $\pm 20\%$.
- ii) The ultraviolet DIAL system was used to monitor the emission rates and concentrations of sulphur dioxide produced from combustion and emitted by industrial stacks. These stacks were instrumented with calibrated in-stack sampling instruments. The results of the two sets of measurements agreed to within $\pm 12\%$.
- iii) DIAL Measurements of controlled releases of methane from a stack agreed with the known emission rates to within $\pm 15\%$.

9.7 NPL OPEN-PATH CALIBRATION FACILITY

NPL has also developed and operate a full-scale facility for the calibration of open path monitors, including DIAL. This consists of a 10 m long windowless cell able to maintain a uniform, independently-monitored concentration of a gaseous species along its length as shown in Figure A1.3. This provides a known controlled section of the atmosphere with traceable concentration over a defined range (10 m). The absence of windows removes reflections and other artefacts from measurements made using optical techniques, providing a direct way to validate and assess the calibration of DIAL instruments.



Figure A1.3 The NPL 10 m calibration cell.

The calibration facility is windowless with a 1 m diameter, to minimise any beam reflections from the cell walls and ends. At each end of the cell is an annular calibration-gas feed ring with multiple outlets injecting the calibration gas mixture into the cell. A ring of tangential fans around the centre of the cell extract gas and entrained air is pulled in through the open ends of the cell. This ensures the backscatter in the cell approximates to the ambient air conditions. Each fan has a long exhaust tube to avoid recirculation of the gas into the cell.

The facility provides the ability to generate a defined concentration path and so it also provides range-resolution validation for DIAL and lidar instruments. The system was used to validate the DIAL with a number of measurements of propane and methane.

10 APPENDIX 2: VOC SPECIATION USING PUMPED SORPTION TUBES

The DIAL measures C2+ VOCs by measuring the differential absorption of two wavelengths of light. The wavelengths used, at around 3000 cm^{-1} , are chosen to measure, in effect, the C-H stretch in the hydrocarbons for C2 and above. The sensitivity of the DIAL is slightly different for different hydrocarbons, and for example an oxygenated hydrocarbon will give a different absorption per mass than a straight chain alkane. The differential absorption strength used in the DIAL VOC measurements was calibrated to give a mass emission rate for gasoline vapour. A different 'cocktail' of hydrocarbons could give a slightly different response per unit mass. Air samples were taken at locations which would provide an indication of the actual speciation of the emission fluxes sampled by the DIAL. If the actual (relative) composition is known from the air sample analyses, then it is possible to check that the absorption coefficients used are appropriate for the actual hydrocarbon mixture present, and adjust the coefficients if necessary.

Air samples were taken at a total of 4 locations around the tank farm site over the course of the measurement campaign. Figure A2.1 show the locations of each numbered sample. The air samples were taken using pumped Perkin Elmer Automatic Thermal Desorption (ATD).

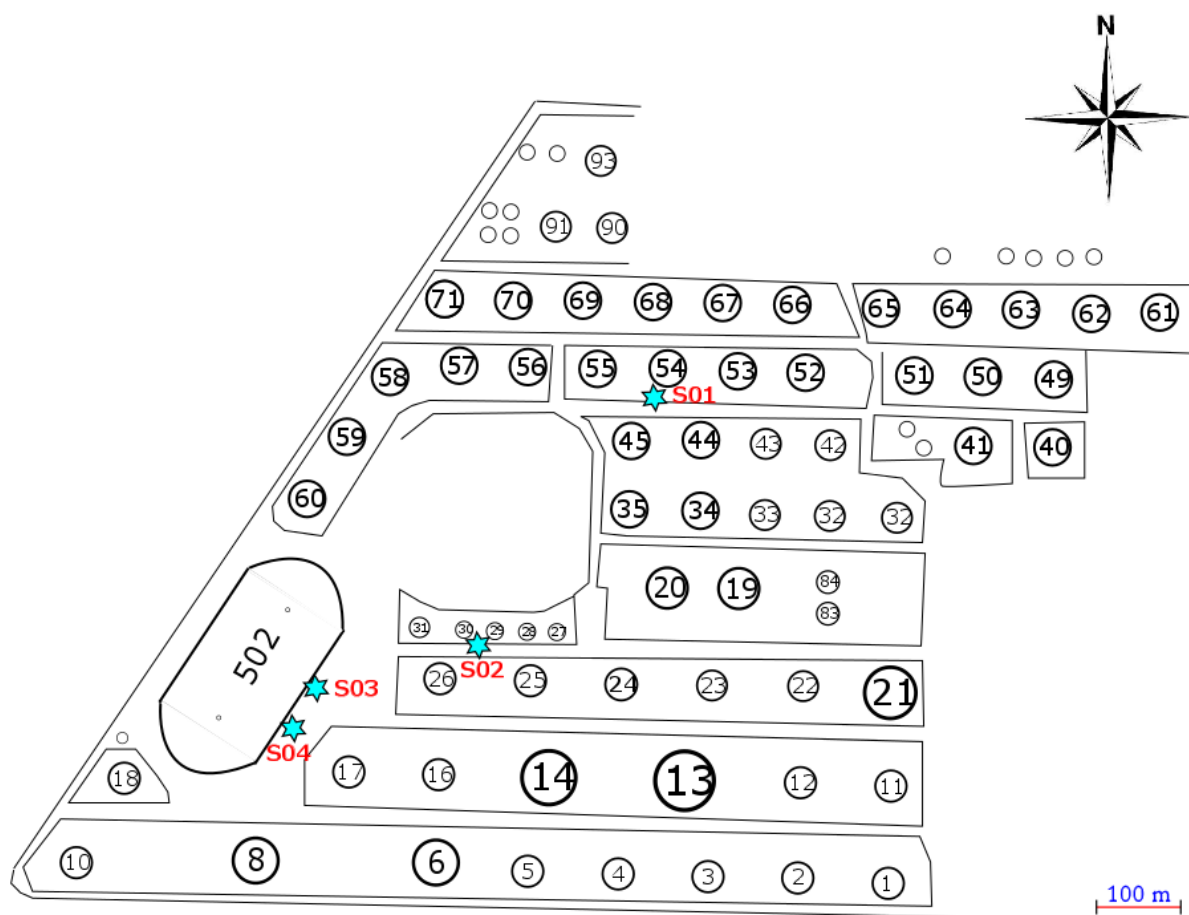


Figure A2.1 Pumped sample tube locations during the campaign.

The ATD tubes were sampled at a flow rate of 40 ml/min to enable a reasonable duration of sample to be taken – typically 30 to 40 minutes. The samples were taken at a height of approximately 2m by mounting the sampling array on a tripod.

The sampler tubes were approximately 6mm in diameter and 90mm long. The sampler tubes contained approximately 200 milligrams to 300 milligrams of sorbent. Three sorbent tubes were used: a carbon molecular sieve (CarboSieve S3) to measure the lightest species, and two in series containing different sorbent materials, a porous polymer (Tenax TA) and a carbon black (Carbopack X). Different sorbents

are needed to cover the diverse boiling point ranges and chemical functional groups of VOCs, and this combination gives a maximum Carbon number range of C₂-C₂₂.

10.1 SPECIATION RESULTS FROM THE ATD TUBE SAMPLES

The tube analyses were carried out by NPL's in house accredited analysis laboratory. Different methods of analysis were used for the CarboSieve S3 and Carbopack X (light hydrocarbons) tubes and the Tenax (heavy hydrocarbons) tubes.

The CarbonSieve S3 and Carbopack X method of analysis was based on EN ISO 16017-2 and was carried out using UKAS (United Kingdom Accreditation Service) accredited method QPDQM/B/526. This method combines Automatic Thermal Desorption with Gas Chromatography (GC), with a Flame Ionisation Detector (FID).

The analysis instrument used is an Automated Thermal Desorber autosampler coupled to a Gas Chromatograph usually with a flame ionization detector. The VOCs are released from the sampler tube using a heated oven in an inert gas stream of helium. The VOCs are refocused onto a small cold trap prior to transfer onto the gas chromatography column. Generally a coated fused silica gas chromatography column of diameter 320 micrometers and length 60 meters is used to separate the individual VOCs collected. Using VOC standard materials, the identification of the individual VOC components are compared to the column elution time (retention time) of the standard VOC materials. The mass of VOCs collected is quantified using the flame ionization detector. A series of calibrations standards are used to calibrate the flame ionization detector response. The concentration of the VOC in ambient air is then calculated using from the mass collected and the volume of air sampled.

A similar procedure was used for the Tenax analyses, but in this case mass spectrometric (MS) detection was used after the GC separation instead of a FID. MS detection provides additional information on the mass of ionized fragments from the different species while retaining the elution separation of the gases, which assists in the species identification within the potentially complex mixture of heavy organic components.

Over 30 different VOCs were identified in the four samples and to simplify the presentation of the data the aliphatic species have been separated into saturated and unsaturated compounds and then grouped by carbon number (from C₂ to C₁₂), and the aromatic species have also been grouped together. The results for the selected samples are given in Figure A2.2.

The results show that the observed VOC mixture covers a wide carbon number range (up to C₁₀). Samples S01 and S02 were representative of the emission from the tanks area while samples S03 and S04 were representative of the emission from Reservoir 502. As highlighted above and in Section 8.4, the DIAL VOC measurement is targeted on C₂+ hydrocarbons with a standard absorption coefficient based on gasoline vapour. For these tube measurements, the scaling factors to go from the standard DIAL VOC coefficients to the measured tank farm area and Reservoir 502 averaged mixtures were 1.09 ± 0.04 and 1.34 ± 0.05 respectively.

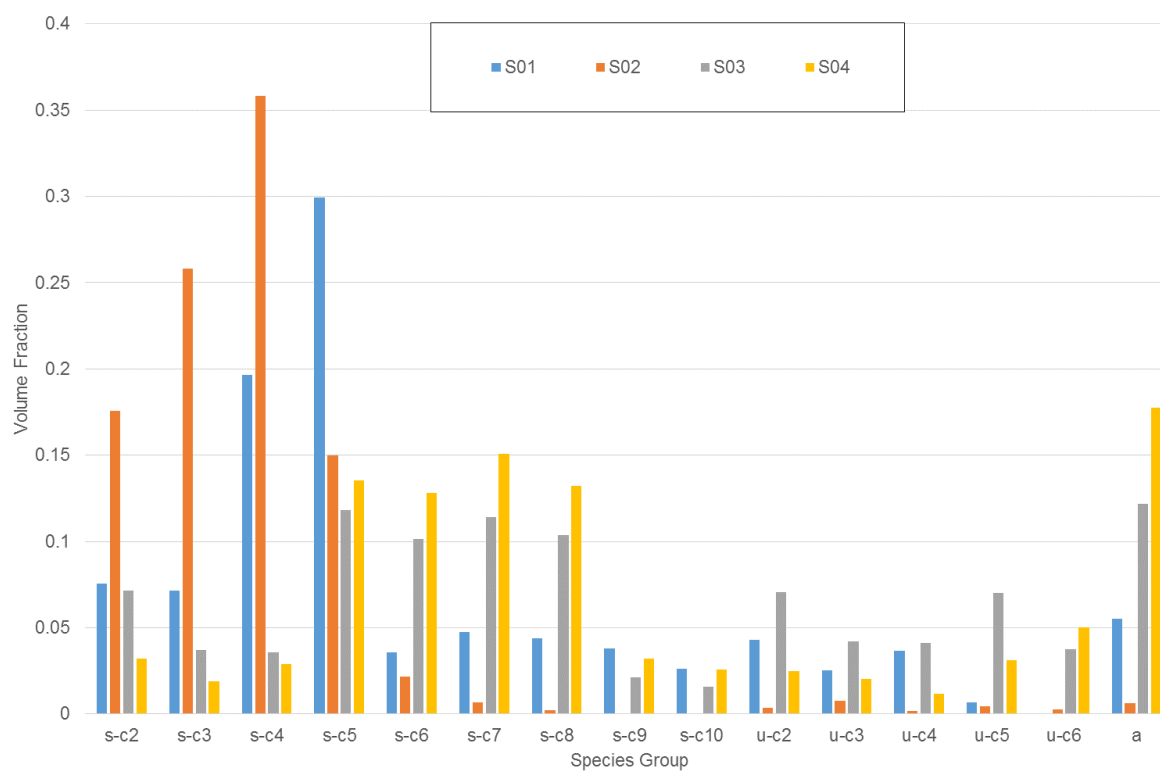


Figure A2.2 Volume fraction of VOCs in the four samples.